



**PULSED ULTRAVIOLET LIGHT EMITTING DIODES FOR
ADVANCED OXIDATION OF TARTRAZINE**

THESIS

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Abstract

A study was conducted to evaluate the advanced oxidation of organic contaminants using pulsed ultraviolet light emitted diode (UV LED). Tartrazine was used as a surrogate organic compound. Low pressure Mercury-based lamps currently used in the treatment of water pose potential health risks if broken and create final disposal issues at the end of their service life. UV LED offers an alternative solution due to its non-toxicity, flexible design, and longer operating life compared to the mercury-based lamps. The apparent first order reaction rate constant for tartrazine degradation increased linearly with increasing duty cycle. At a continuous 100% duty cycle, tartrazine degraded by 18% after 5 hours of operation. When normalized to power output, the lower duty cycles exhibited greater rate constants. The 5% duty cycle produced a normalized rate constant 100% greater than those observed at 20% and higher duty cycles. Reduced LED power output with time was not observed. As an anionic compound, it is believed tartrazine sorption to the LED surface was not occurring. Believed to be due to incomplete reactor mix, the experimental results show increased data noise at duty cycles 20% and greater. When the reactor was equipped with a mechanical mixing device, the data scatter was considerably reduced. Root square mean, R^2 , significantly improved from 0.57- 0.96 range for non-stirred reactor to 0.70 - 0.99 range for stirred reactor between 5% to 100% duty cycles.

To my Wife and Children

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Patrick M. Mudimbi

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PULSED ULTRAVIOLET LIGHT EMITTING DIODES FOR ADVANCED OXIDATION OF TARTRAZINE

I. Introduction

Disposition of liquid waste poses a unique challenge as some wastes contain chemicals that may be difficult to treat or may disrupt the wastewater treatment plant's performance. The Environmental Protection Agency (EPA) has been investigating the use of advanced oxidation processes (AOPs) with the use of UV LED to oxidize the liquid waste prior to sending them to the treatment plan. AOP is a chemical process designed to remove organic and some inorganic compounds in water using ozone, hydrogen peroxide and UV light to generate hydroxyl radicals which disinfect water.

The use of AOP in wastewater treatment is appealing because it can remediate a wide range of organic pollutants and some inorganic contaminants at near ambient temperature and pressure (Munter, 2001). Additionally, AOP can significantly reduce the concentration of pollutants from several hundred ppm to less than 5 ppb (Munter, 2001). In recent years, there has been a growing interest in LEDs, because they do not require filament, and can burn easily, in comparison to the incandescent bulbs. Furthermore, LEDs utilize a significantly lower amount of energy while lasting considerably longer than the conventional lamp.

Recently, an experiment on AOP with a UV LED reactor was conducted using methylene blue as an indicator dye to measure the hydroxyl radicals' generation. Methylene blue is known for its ability to undergo photo-catalytic degradation, which can be used to measure the degradation of hydrogen peroxide (Tayade et al., 2009). This research is intended to evaluate the performance of a pulsed UV LED reactor in the degradation of tartrazine with AOP/H₂O₂, and to investigate data scatter phenomena observed in results from previous experiments on MB

II. Literature Review

2.1 Advanced Oxidation Process (AOP) with UV LED

AOP has been practiced for decades in the removal of pollutants in drinking water and the treatment of contaminants in wastewater and groundwater (Glaze et al. 1987). AOP is a water treatment process which involves the production of hydroxyl radicals sufficient enough to have an impact on water purification at near ambient temperature and pressure (Glaze et al. 1987).

Hydroxyl radicals (OH^\cdot), generated from decomposing peroxide or ozone in AOP, are very aggressive and powerful oxidants that readily react with most organic compounds. The destructive effects of OH radicals are made possible due to the presence of oxygen contained in a contaminated substance. There are two major categorical AOP methods: non-photochemical and photochemical (Munter, 2001).

2.1.1 Non-photochemical methods

There are approximately four non-photochemical methods involved in the production of hydroxyl radicals which do not require electromagnetic stimulation. The first method involves the reaction with ozone molecules at an elevated pH; hydroxide ions and ozone react to form oxygen molecules and hydroxyl radicals (Gottschalk et al, 2000). The second is the peroxone method; ozone and hydrogen peroxide undergo different reaction steps to generate OH radicals (Hoigne et al, 1982). Combining ozone and hydrogen peroxide proved to perform better than using ozone alone in the degradation of pesticide in the water (Paillard et al, 1988). The third method is the combination of ozone and a catalyst to accelerate the decomposition of target compounds such as chlorobenzenes in wastewater (Cortes et al, 1998). This method is also more

efficient than ozone with high pH in reducing total organic carbon (TOC) and chemical oxygen demand (COD) from wastewater (Cortes et al, 1998). The fourth method is the Fenton system ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) combination, which consists of hydrogen peroxide combined with ferrous ion (Fe^{2+}) to generate hydroxyl radicals (Fenton, 1884). The Fenton system is an attractive method in soil and wastewater treatment due to the abundance of iron in nature and the availability of hydrogen peroxide. However, while Fenton is also very effective in generating hydroxyl radicals, it requires a high Fe^{2+} concentration to achieve this result.

2.1.2 Photochemical methods

In many cases, the oxidation of organic compounds is not complete. Certain compounds are resistant to degradation via ozone and H_2O_2 unless there are assisted with a UV radiation. Photochemical methods have been shown to enhance the degradation of organic compounds in the presence of a UV power source. In February 2001, Munter listed five photochemical methods that can be used to improve oxidation. The first photochemical method is the ozone-UV radiation method. In this method, the absorption of UV light by ozone is optimal in the generation of hydroxyl radicals when stimulated with UV energy having a wavelength near at 254 nm. However, it is expensive to generate enough OH radicals using the low pressure mercury lamps to generate illumination at this wavelength. Therefore, the second method involved a direct photolysis of H_2O_2 to generate OH radicals. This process was used by Bischof et al., 1996, to demonstrate that atrazine, desethylatrazine, and simazine molecules can be mineralized efficiently to carbon dioxide in a solution containing H_2O_2 and a UV source. This method has been under investigation for the disinfection of water. The third ($\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$), fourth (Photo-Fenton and Fenton-like systems), and fifth (UV/TiO_2) methods use the same principle; they involve the use of an oxidant or a catalyst with a UV source to generate OH radicals.

2.2 AOP with UV LED

UV irradiation can be used to inactivate pathogenic cells. Most cell molecules absorb UV energy and are maximally vulnerable to energy with wavelengths near 260 nm (Jagger 1967). In this region of the electromagnetic spectrum, the absorbed energy may cause sustainable damage to the strands of DNA molecular and impairs its ability to reproduce.

For decades, common low pressure mercury lamps were used as the UV energy source in the disinfection process due to their ability to generate energy with a wavelength of 253.7 nm. However, mercury lamps contain mercury vapors which pose serious human health risks and environmental concerns. Long term exposure to mercury vapor may have negative effects on the reproductive system, nervous system and other vital organs and lead to severe damage to these organs, resulting in death (OSHA, 2012).

LEDs are promising alternatives for UV energy sources. Contrarily to mercury lamps, LEDs has the potential for low power requirements, which is more efficient for the conversion of electrical power into UV light. Furthermore, LEDs are robust and compact; they have no warm-up time, no disposal problems, and offer a long lifetime (Olivier et al., 2012). Furthermore, LEDs offer more flexibility in selecting desired frequency capable of affecting a broader spectrum of antimicrobial agent. Table 1 shows that in a long run LED has superior advantage in longevity, efficiency, operating temperature, and electrical output over low pressure lamp and medium pressure lamp.

Table 1 UV Lamp Properties

Table 1 UV lamps properties. Adapted from Ibrahim (2012)			
	Low pressure lamp	Medium pressure Lamp	LED (Predicion 2020)
Typical wavelength	Monochromatic 254 nm	Polychromatic 200-500 nm	Any from 240 nm
Wall plug efficiency (%)	35-38%	10-20%	75%
Lifetime (h)	8000-10000	4000-8000	100000
Electrical input (w)	8-100	100-60000	1
Operating temperature (oC)	40	600-900	20

Additionally, because LEDs interrupt the DNA of microorganisms without the introduction of added chemicals, there are usually results in minimal disinfection byproduct generation, hence posing insignificant human health hazards or environmental risks. Although LEDs are still in developmental stages, they have been tested effectively in the inactivation of several microbial pathogens such as bacteria in food poisoning (Hamamoto et al, 2007), bacillus subtilis spores (Würtele et al, 2011), and E. coli in water (Chatterley and Linden, 2010).

2.3 UV LED Pulsing

Results from previous studies suggested that pulsing UV energy can be used in the disinfection of pathogens. Pulsing UV energy causes photophysical stress damage due to the disturbance endured in cellular membranes (Wengraitis et al, 2012). Krishnamurthy and Irudayaraj's (2010) study on *Staphylococcus aureus* disinfection indicated that UV pulsing has double the effects on a cell; it disabled the microbial cell from replicating and damaged the cell structures from repeated disturbance from pulsing. Further researches have been performed to exploit the effectiveness of UV LED pulsing in the disinfection of pathogens. At ultraviolet –C (UV-C) range of (100-280 nm), LEDs offer various pulse repetition frequencies (PRFs), pulse

length, and duty cycles at a very low power requirement. In 2007, Hamamoto et al. studied *E. coli* disinfection with continuous-wave (CW) UV LEDs emitting at 365 nm. Results showed a reduction in *E. coli* population by 5.7 log units after 315 J cm⁻² of 365 nm exposure. Li et al., 2010, performed a study on *E. coli* and *Candida albicans* with pulsed UV LEDs at various PRFs (0.1, 1, 10, 100, 1000 Hz and CW) and duty cycles (25%, 50%, 75%, and CW). At 100 Hz, PRF yielded the highest sensitivity for the *E. coli* and *Candida albicans* disinfection, and the pulsed sensitivity was optimum at 25% with 5.2 log units higher than CW. A very similar method was used by Wengraitis et al., 2012, to disinfect *E. coli* with pulsed UV-C radiation from LEDs emitting at 275 nm wavelength. Findings revealed that sensitivity decreased as duty cycle and PRF increased, pulsed sensitivity was 3.8 log units higher than CW, the disinfection was optimum at 1 Hz 10% duty cycle, and *E. coli* was more sensitive to 272 nm radiation than to 365 nm radiation.

2.4 Chemical Degradation with UV/ H₂O₂ AOP

Throughout the years, the use of UV AOP in the disinfection of pathogens has been very promising; however, there are still other organic contaminants that are very difficult to remove using these conventional methods. Researchers have been exploring the possibility of degrading these hard to destroy organic contaminants using UV/ H₂O₂ AOP. Baldyga and Bourne (1999), Spalding (1998), Marchisio and Barresi (2003) discovered that the degradation of organic contaminants by UV AOP occurs through a complex chain of chemical reactions. The byproducts resulting from these reactions are highly sensitive to the UV fluence rate and to the mixing and turbulence rate in the reactor. Bolton (2001) described that, in a UV reactor, fluence rate is the total radiant power incident from all possible directions of the light onto an

infinitesimally small sphere of a cross-sectional area dA , divided by dA . The fluence rate depends on the absorptive characteristics of the media and the distance from the lamp, which contributes to the effectiveness of $OH\cdot$ production in the UV reactor during AOP.

2.4.1 Degradation of organic contaminant with Low-pressure UV/ H_2O_2 AOP

Alpert et al. (2009) studied the performance of the computational fluid dynamic (CFD)/UV/ H_2O_2 AOP in the degradation of organic contaminants. CFD is a technique used to describe the physical and chemical changes within a reactor through space and time. Methylene blue (MB) was the organic indicator dye used in lieu of actual organic contaminants for this study. Results exhibited that MB removal depended on the concentration of dissolved organic carbon (DOC) present in the water matrix. At zero DOC concentration, 0.0 mgL^{-1} , MB had diminished by 94.1%, and at DOC concentration of 2.0 mgL^{-1} , only 70 % MB elimination was achieved. DOC, alkalinity, and chloramines are known as scavengers, because they consume hydroxyl radicals and lower the effectiveness of UV AOP to degrade chemicals (Alpert et al, 2009). MB removal depends strongly on the reaction between MB and the available hydroxyl radicals produced.

2.4.2 Degradation of organic contaminant with pulsed UV LEDs

Limited studies have been completed to evaluate the effects of pulsed UV LEDs in the degradation of organic contaminants. Capt Duckworth (2013), a graduate from AFIT, studied the effects UV LED pulsing and continuous power in the advanced oxidation of MB. UV LEDs were pulsed at 5%, 10%, 30%, 50%, 70%, and 100% duty cycles. Duty cycles are LED percent output power control signals generated by a computer program, i.e. DASYLab (DASYLab, version 12, Stamford, CT), such that 5% duty cycle means that LEDs are powered on for 5.5 milliseconds (ms) and then powered off for 104.5 ms, 10% (11 ms on, 99 ms off), 30% (33 ms on, 77 ms off),

50% (55 ms on, 55 ms off), 70% (77 ms on, 33 ms off), and 100% means that the signal is continuous. Duckworth's (2013) study results indicated that MB AOP is an apparent first-order degradation rate constant that increases linearly with duty cycle. The LED output power emission decreased over the time of use with the LEDs. The reduction in LED output power over time was mainly due to the fouling effect of the LEDs; fouling degraded the LEDs power output by 40% after 75 hours of use. Fouling was caused by the anionic property of LED, which attracted the cationic MB from the solution and gradually formed film on the LED silicate glass surface, altering the UV LEDs output power over time. Further, the results also revealed cyclic patterns between 10% and 70% duty cycles. These patterns were believed to be caused by incomplete mixing within the UV reactor.

2.4.3 Tartrazine

Tartrazine is an organic pollutant widely used in the food and pharmaceutical industries. Tartrazine causes allergic reactions in some individuals; the European Food Safety Authority (2009) reported doses of 7.5 mg/kg are toxic to humans. There have been several types of health concerns reportedly linked to tartrazine like, hypersensitivity, skin eczema, immunosuppressive effects, allergy and asthma, mutagenic and carcinogenic effects (Sushmita et al., 2013). Al-Dawery (2013) studied the effects of photo-catalyst degradation of tartrazine in wastewater using titanium dioxide (TiO_2) with a UV lamp being used as the source of UV light. The results showed that Tartrazine degradation also followed first order reaction rate constant like MB; the maximum rate of degradation was $3.4 \times 10^{-3}/\text{min}$ in a solution of 500 mg/L TiO_2 . This research further showed that a slight change in pH occurred during the reaction but did not have a significant impact on the photo-catalyst process. Further, tartrazine is an anionic dye (Sushmita et al. 2013), and was purposely selected for this research to avoid potential fouling effect

observed in MB experiment. The positively charged silica glass surface of the LED should repeal the negatively charged tartrazine, minimizing potential filming on the LED surface.

III. Research Objectives

The overall goal of this study is to assess the degradation of tartrazine/ H_2O_2 using AOP with UV LEDs as the power source for the purpose of characterizing LEDs for the degradation of organic contaminants in the water. The specific tasks are:

- i. Determine the effect of the UV LED duty cycle on the degradation of tartrazine in terms of an apparent rate constant and an apparent rate constant normalized to duty cycle
- ii. Measure LED power reduction as a function of operating time with an anionic surrogate organic compound and compare effects to previous work using a cationic organic compound, MB.
- iii. Investigate the effect of mechanically mixed reactor on the performance of the UV LED reactor and compare these findings to the results obtained from the non-stirred reactor

IV. Materials and Methods

Hydroxide radicals are generated through direct photolysis of hydrogen peroxide with UV light. Hydroxide radicals instantly react with tartrazine and destroy its molecular structure. The destruction of Tartrazine can be measured colorimetrically, and may serve as a benchmark for degrading other organic contaminants. Tartrazine was selected in this research because it is an ideal surrogate for other recalcitrant organic chemicals that may be found in military water and wastewater. A total of seven experiments were conducted, two of which were control experiments. The first control involved a 0% duty cycle (no UV energy) and 5mM hydrogen peroxide. The second control involved a 100% duty cycle (continuous UV energy) and no hydrogen peroxide. At 0% duty cycle, the LEDs were turned off, and a solution containing tartrazine and hydrogen peroxide were pumped into the UV reactor to determine if the reaction would take place in the absence of UV stimulation. At 100% duty cycle, LEDs were on constantly; a solution containing only tartrazine was forced into the reactor to determine if it will undergo degradation without the presence of H₂O₂. Five experiments were conducted at several duty cycles each, with three experiments repeated at the same solution rate of 1.45 ml/min, without any mechanical stirring. The fourth was conducted at a half reactor rate of 0.7 ml/min. The last experiment incorporated a stirring device for mechanism mixing, with a reactor rate of 1.45 ml/min. The study was conducted at the following duty cycles: 5%, 10%, 20%, 30%, 50%, 70% and 100%. All experiments were completed using the same LEDs and UV reactor. The methodology section will cover the experiment design specifics and configuration, data collection method, and analysis.

4.1 Design specification and configuration

Seven LEDs were utilized in this experiment. The LEDs (Sensor Electronic Technology, Inc) were previously used during a MB experiment conducted by Almquist (2014). After the experiment was over, layers of MB were observed on the quartz of the LEDs lenses; this reduced the LEDs output power considerably. The stained LEDs were gently cleaned with a methanol wipe and the output power was restored to its original setting before they were reused. The wavelength emitted averaged 245 nm and the power emitted averaged 0.4 mW after cleaning. The LEDs were all positioned on one side plate of the reactor, Figure 1, such that the UV irradiation can be evenly distributed to prevent any dead zone.



Figure 1 - UV reactor with LEDs positioned on one side plate

The reactor is a modified stainless cylindrical pipe with 350 mL volume. The diameter and length of the reactor were all three inches. The two ends of the pipe were covered with stainless steel plates to form an enclosed cylindrical tube, then properly sealed with liquid silicon to prevent water infiltration. To allow fluid to flow in and out of the tube, one-inch diameter stainless pipes were connected on the opposite sides of the tube. The fluid was propelled into the tube by a pump (MasterFlex Condole Drive, model number 77521-50, Gelsenkirchen, Germany)

at a rate of 1.45 mL per min through a 0.8 mL diameter inner tubing (PharMed BPT, Valley Forge, PA). All LEDs were positioned on the plate closest to the outflow pipe, so that most degraded tartrazine/H₂O₂ solution is sent to the spectrophotometer for measurements. The Agilent Technologies Cary 60 UV-Vis spectrophotometer is an efficient and accurate instrument capable of scanning a larger wavelength range (190-1100 nm) with a scan rate up to 24,000 nm per minute (Agilent Technology). Cary 60 UV-Vis was used to measure the absorbed light of the degraded tartrazine at 430 nm wavelength (J. Maslowska, 1996) as it passed through a small glass tube.

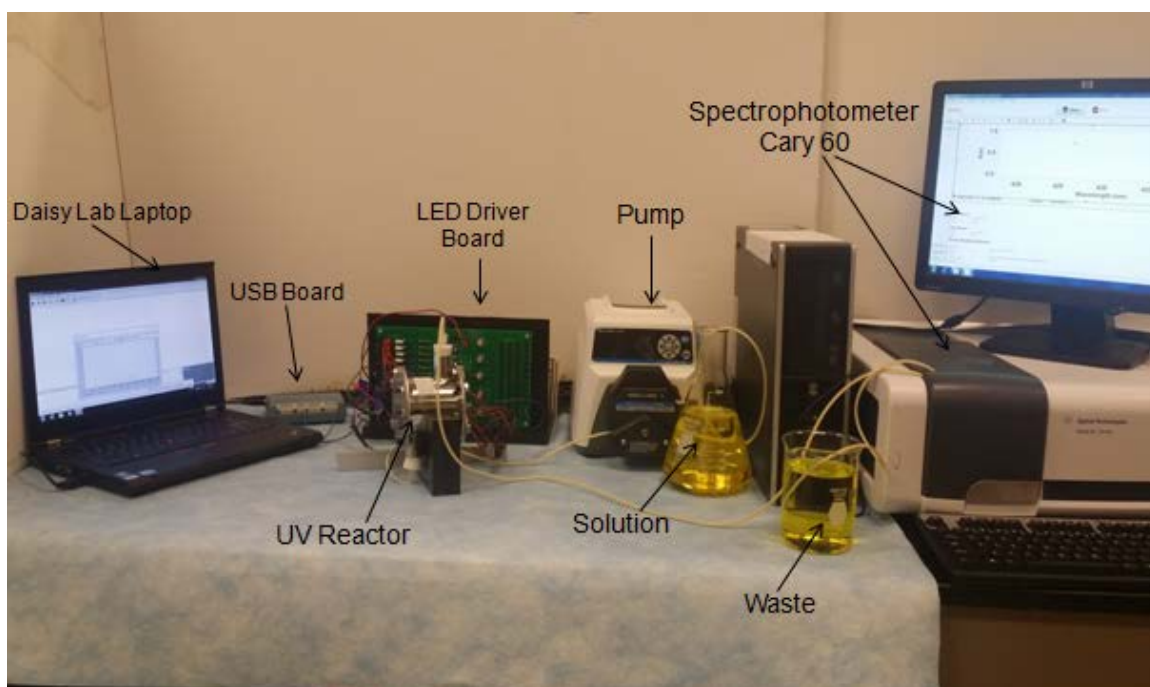


Figure 2 - Tartrazine experimental set up

The UV LEDs were powered by a circuit driver board designed by the research advisors. The driver board is comprised of a constant current driver and an operational amplifier (op-amp). The constant current driver (DynaOhm 4006-020 1338, Randolph, VT) is a semi-conductor-based resistor that allowed a constant current of 20 mA to each LED in the reactor and prevented

negative current flow. Preventing feedback loop was important because it may cause negative voltage in the circuit and damage the LEDs. The Op-amp Data Acquisition Module (USB 2408-2AO) is a multi-function electronic hardware driver box that was used to provide voltage which served as a control signal to the circuit driver board. The data acquisition module provided voltage and signals generated by a computer software program called DASYLAB (DASYLAB, 2014).

DASYLAB programs were designed and installed into the faculty Laptop to generate continuous and pulsing signals. Although, the DASYLAB was programmed for several different pulsing signals (i.e. 5%, 10%, and 20%), only one signal output was generated at a time and all pulsing generated a frequency of 9.09 hertz. The signals were sent to the driver box for processing and then sent to the driver board. The output signal from the driver box was limited to 10 volts. An oscilloscope (WON PDS50221) was used to validate the intensity of the continuous and pulsing signals originated from DASYLAB at the driver box junction. The oscilloscope was also used at circuit driver board junction to validate the voltage going through each LED in the reactor.

4.2 Procedures

The reactor was filled with a well-mixed solution containing 26.7 mg per liter tartrazine, 2.88 g H_2O_2 and 1000 mL distilled water and pumped continuously through reactor. The effluent was sent to the Agilent Technologies Cary 60 UV-Vis at a constant rate of 1.45 mL per minute. The spectrophotometer was programmed to take measurements every five minutes for five hours at a tartrazine target wavelength of 430 nm. The measurements were input into an excel program and graphed to create a visual aid representation of tartrazine degradation at

different duty cycles. Measurement procedures and parameters, such as rate, measurement frequency, and reactor volume, were selected to maintain consistency with previous experiments conducted by Duckworth (2013) and Almquist (2014) for comparison purposes. However, per EPA request, to better characterize the LEDs, the number of duty cycles, reactor flow, and mechanical mixing of the UV reactor remained unchanged.

4.3 Effect of duty cycle measurements

Duckworth completed four experiments on MB degradation with pulsed UV LEDs reactor; five trials were completed at a 100% duty cycle, three at 10%, three at 70%, and four at 50%. The results left several knowledge gaps regarding the performance of the UV reactor at lower duty cycles and the data was scattered at some duty cycles. It was believed that the order the duty cycles were completed could have impacted the results. To investigate this matter, Almquist repeated the experiment with randomized duty cycles and reversed the order on the next experiment. Further, Almquist examined the effect of 5% and 30% duty cycles on the MB degradation. Similar results were obtained, consequently, the scatter data was attributed to incomplete mixing of the reactor. The effect of duty cycles on tartrazine degradation was evaluated at 5%, 10%, 20%, 30%, 50%, 70%, and 100% duty cycles. 20% duty cycle was included at the second and consecutive experiments per EPA request. The two control experiments mentioned earlier were conducted at 0% and 100% duty cycles to ensure that no other factors affect tartrazine degradation except for the hydroxyl radicals produced by the AOP.

4.4 Modeling the reaction

A reaction model was developed by the AFIT faculty to evaluate the AOP of Methylene Blue/H₂O₂ inside the UV LED reactor. The same model was used for the AOP of Tartrazine/H₂O₂ with a pulsing UV LED reactor. The model assumed that the reactor would behave as an ideal continuously stirred tank reactor (CSTR). The volume of the reactor was 350 mL and the reactor flow was 1.45 mL/min, then it was reduced to 0.7 mL/min. The reaction is pseudo-first-order, due to the excess of H₂O₂ compared to the concentration of the dye in the reactor. The concentration ratio between tartrazine and H₂O₂ is approximately 1 to 100. The model was based on a simple mass balance principle (Eq. 1) of fluid entering and exiting the reactor. The relative concentration of the dye (C/C_o) was expanded from the same mass balance equation under the assumption that the reaction is a CSTR. This final model (Eq. 2) was used for all methylene blue experimental data collected by Duckworth, Almquist and colleagues, as well as all tartrazine experimental data obtained in the current effort.

$$\text{Mass accumulated} = \text{Mass In} - \text{Mass Out} + \text{Mass Produced} - \text{Mass Consumed} \quad (\text{Eq. 1})$$

$$\frac{C_T}{C_{T0}} = \left(\frac{1}{1 + \tau k} \right) \left(1 + \tau k e^{-\left(\frac{1}{\tau} + k\right)t} \right) \quad (\text{Eq. 2})$$

Where:

C_T = final concentration of tartrazine

C_{T0} = initial concentration of tartrazine

τ = residence time

k = apparent first-order rate constant

t = reaction time

Based on this model, it was assumed that:

The reactor constant inflow and outflow was 1.45 mL/min

The volume was constant at 350 mL

The reaction is pseudo-first-order

The reactor is an ideal continuously stirred tank reactor (CSTR)

4.5 Data scatter investigations

Two experiments were conducted to investigate scatter in the results observed in previous MB experiments. The first test was conducted to evaluate the impact of flow in reactor disturbance. A computational fluid dynamic (CFD) model by Almquist showed that when the velocity profile increased from 0.0122 ml/s to 0.1 ml/s, the disturbance in the reactor also increased. Therefore, to investigate this disturbance experimentally, a test was conducted at 0.7 ml/s with various duty cycles. The second experiment was conducted to investigate the effect of the reactor mixing in the results. The reactor was mechanically stirred and results were evaluated. Both tests were conducted the same as the previous tests.

4.6 LEDs performance after usage

The performance of LEDs was evaluated after usage. Methylene blue has a fouling effect on the quartz lenses of the LEDs (Duckworth, 2013). The staining affected the results of the experiments as the LEDs intensity had degraded due to the coating that covered the LEDs lens. To minimize a similar effect during tartrazine/H₂O₂ experiments, the reactor was filled with DI water at the end of each experiment; LED lens stayed moist and dry dye didn't stick to the lens. At the end of all three experiments, LEDs were removed from the reactor and measured to

determine their output power, and then cleaned with a methanol wipe to remove potential stain, and measured again.

V. Results and Discussion

5.1 Control evaluation

The research began with two controlled experiments intending to show the dependency of H_2O_2 and LED to produce HO^\cdot in the AOP for tartrazine. The first control experiment was conducted at 0% duty cycle with H_2O_2 being present, as illustrated in Figure 5.1, and results showed no degradation of tartrazine when all LEDs were powered off. The straight horizontal lines indicate that tartrazine did not degrade over the course of time. A second control experiment, shown in Figure 5.2, was conducted when all LEDs were powered on (100% duty cycle) and without H_2O_2 being in the solution; similar results were observed indicating no degradation of tartrazine in a 300 minute run. The two control experiments showed no evidence of HO^\cdot production in the absence of a UV source and H_2O_2 . A calibration curve was also drawn in the beginning of each trial to measure the dye concentration and absorption reading using the spectrophotometer at a wave length of 430 nm. All calibration curves were perfectly fitted to a model, Eq. 2, to determine the rate constants and all corresponding coefficients of determination (i.e. R^2) were at least 0.99.

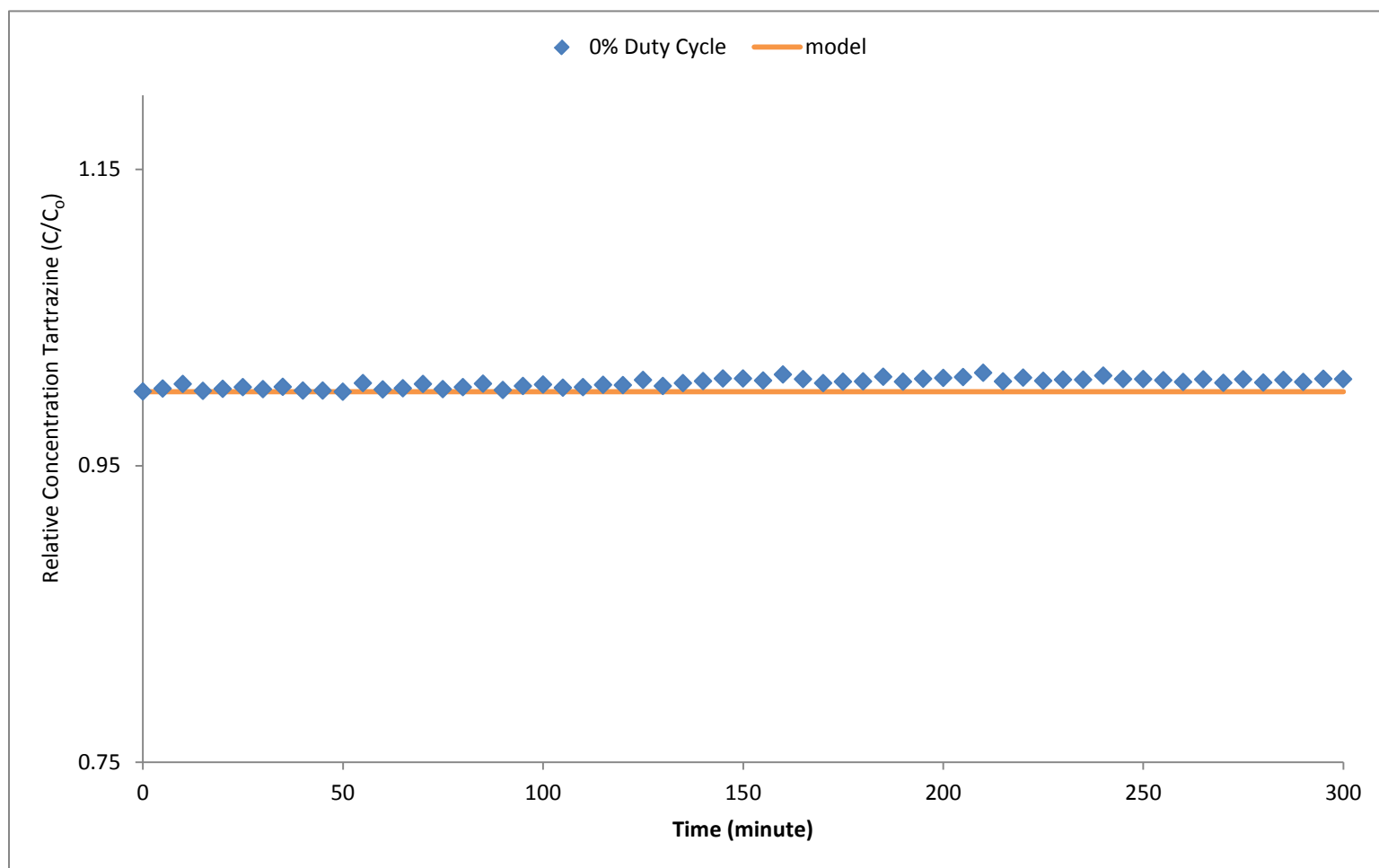


Figure 3 - First Control experiment for tartrazine degradation at 0% duty cycle

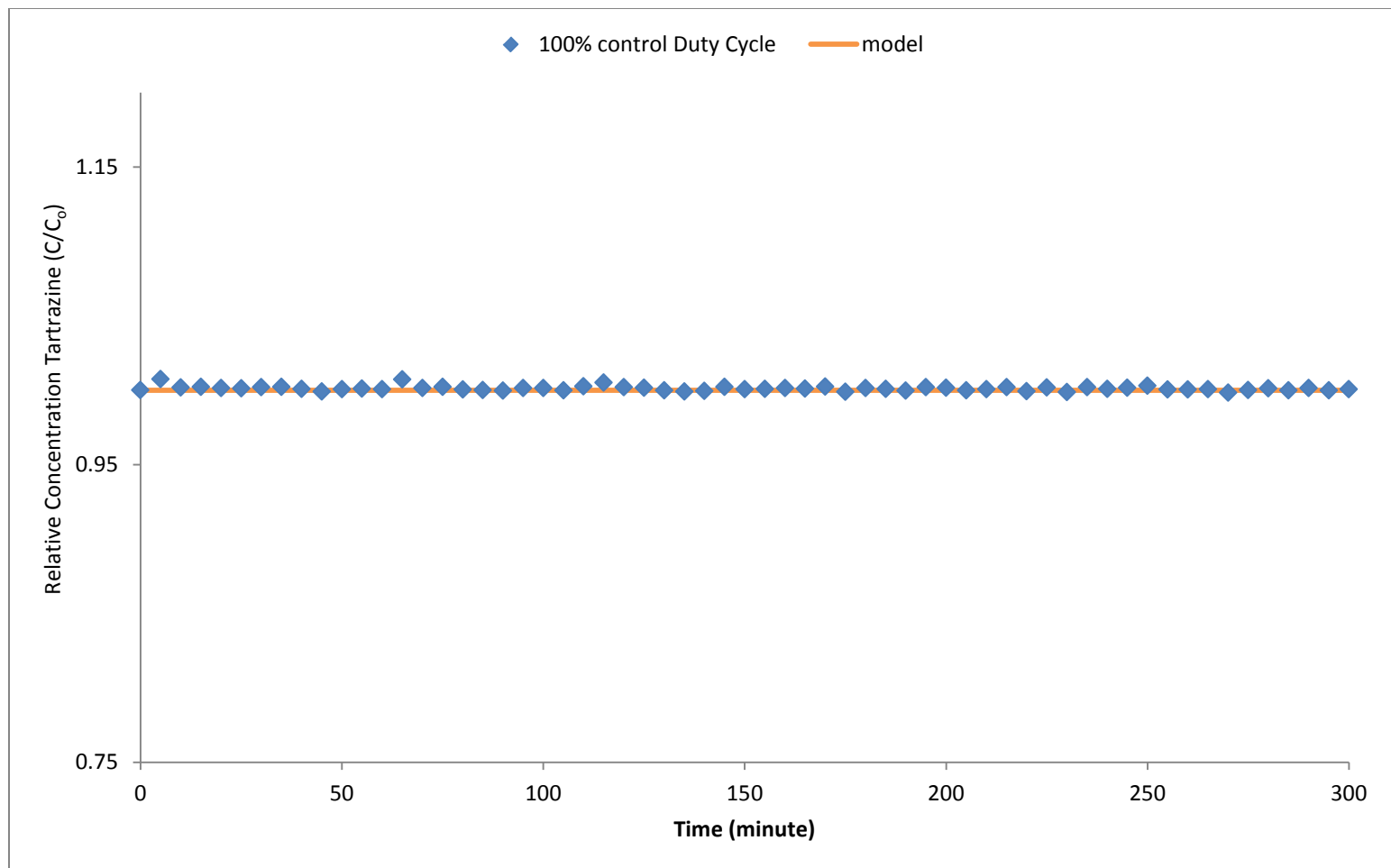


Figure 4 - First Control experiment for tartrazine degradation at 100% duty cycle

5.2 Effects of duty cycles on tartrazine degradation

The results for the first experiment are illustrated in Figure 5.3. The relative concentration of tartrazine (C/C_0) was plotted against time for each pulsed power setting, and the degradation of tartrazine at each duty cycle is represented by the scatter lines and the corresponding fit model by the solid line. As expected, the overall removal of tartrazine increased with the increase of duty cycles. For example, at 10% duty cycle, 13% of tartrazine was degraded in 280 minutes, and at 100% duty cycle 20% was removed in the same timeframe. Similar results were observed in subsequent trials. The second experiment, illustrated in Figure 5.4, also showed similar degradation patterns as duty cycles increased. At lower duty cycles, small degradation is observed, and increased as duty cycles increase. Note that at 100% duty cycle, tartrazine degraded by 17%, lesser than what was observed in the first experiment. Similarly, the third experiment, Figure 5.5, tartrazine degraded by approximately 18%, less than the 20% observed in the first experiment. This is due to the diminishing emission power of the LEDs over time of use observed by both Dr. Almquist (2014) and Capt Duckworth (2013) during MB experiments. A graph of k_s values, representing the destruction of tartrazine, was plotted against effective time of LED usage. As expected, the results, illustrated in Figure 5.6, showed that the apparent rate constant decreases with operation time for some LEDs. At lower duty cycles this phenomena is less pronounced, and was consistent with MB results. As shown in Figure 9, the reduction in LED optical output power was not nearly as great as seen in the MB experimental work. The anionic state of tartrazine is believed

to have repealed the anionic charges on the LED glass surface, preventing tartrazine buildup and output power loss.

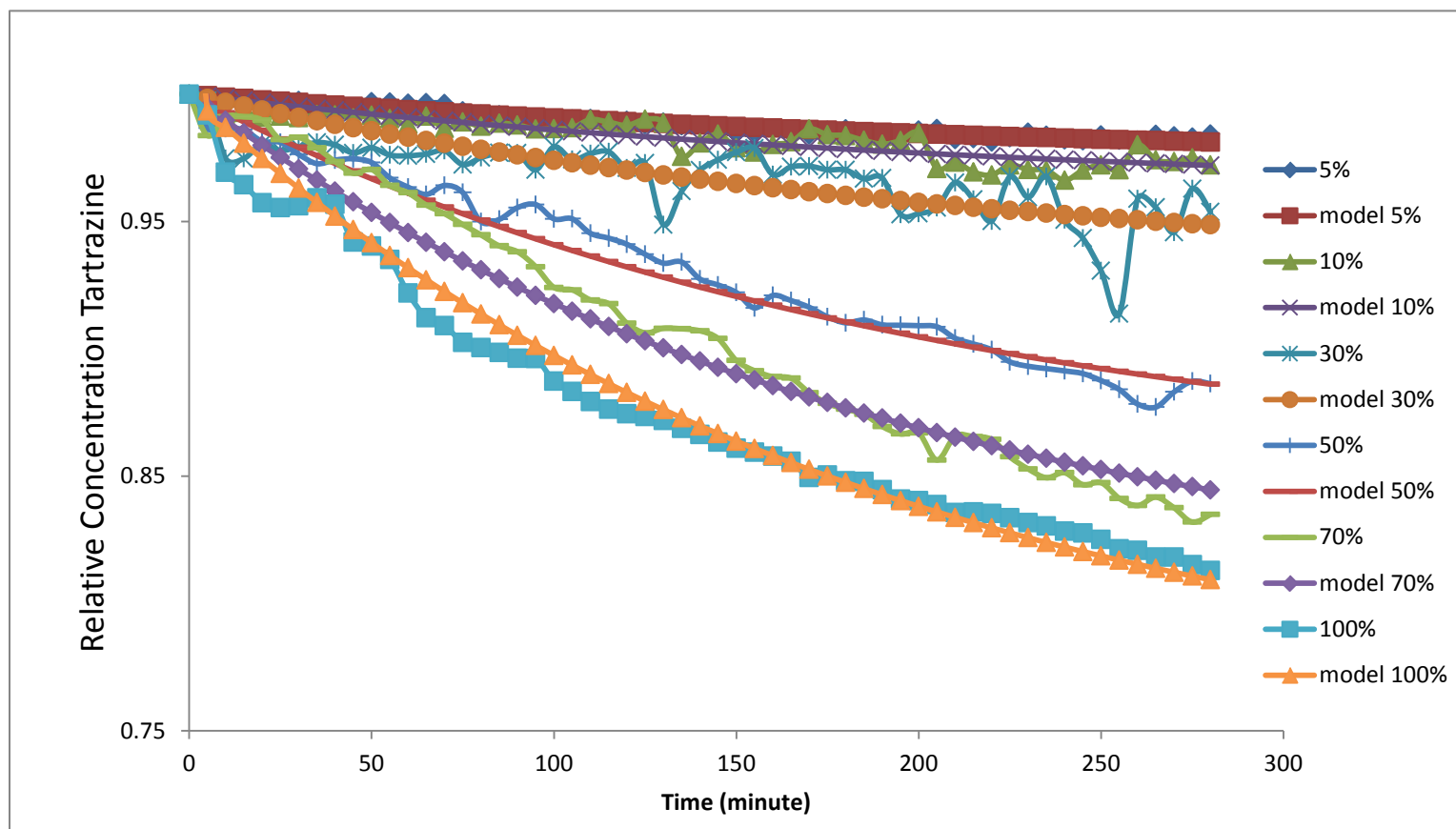


Figure 5 - First trial relative concentration of tartrazine as function of time and duty cycles at 1.45 ml/min reactor rate. Initial concentration (C_0) was approximately 0.05 mol/L tartrazine and 0.005 mol hydrogen peroxide.

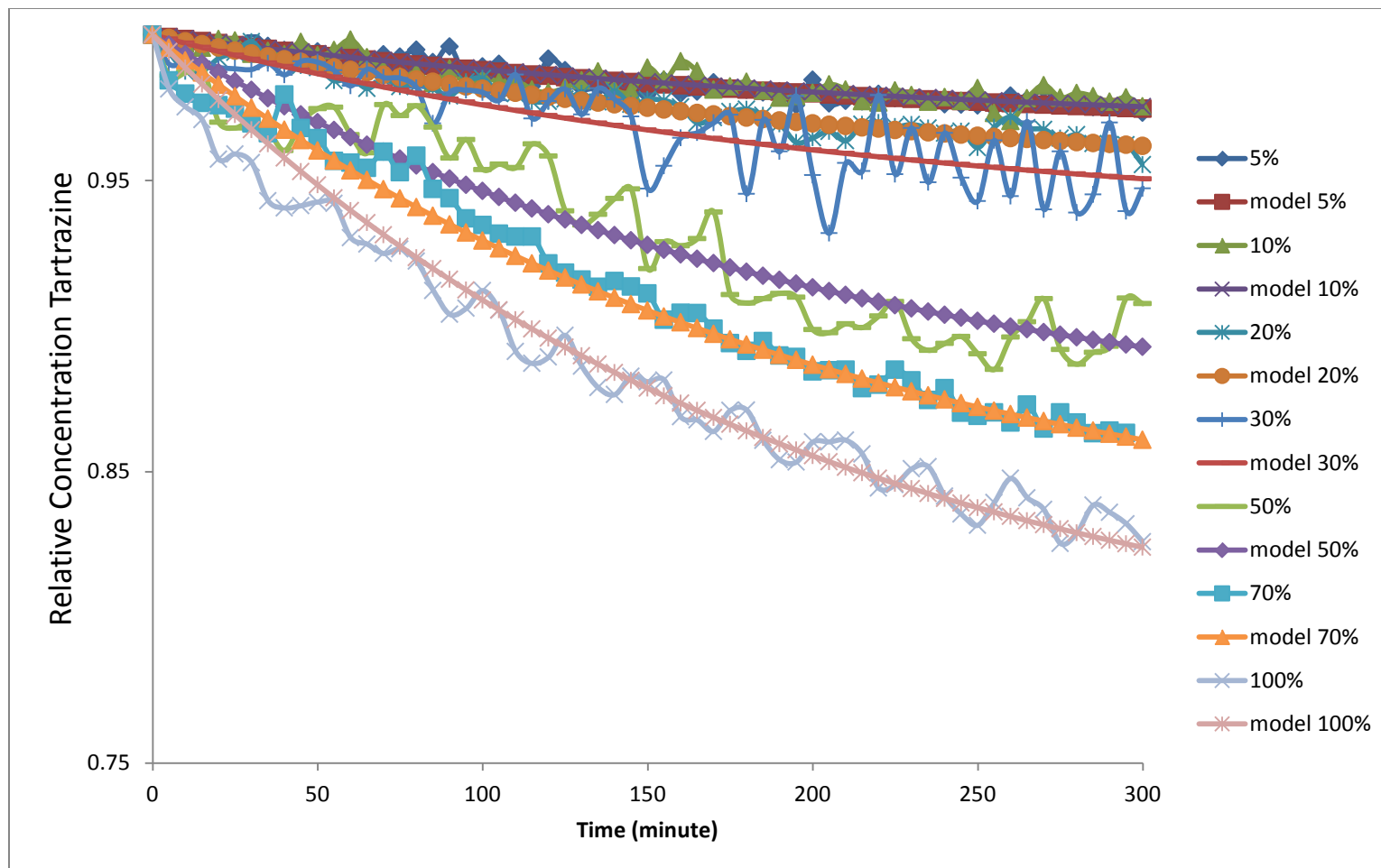


Figure 6 - Second trial relative concentration of tartrazine as function of time and duty cycles at 1.45 ml/min reactor rate.

Initial concentration (C_0) was approximately 0.05 mol/L tartrazine and 0.005 mol hydrogen peroxide.

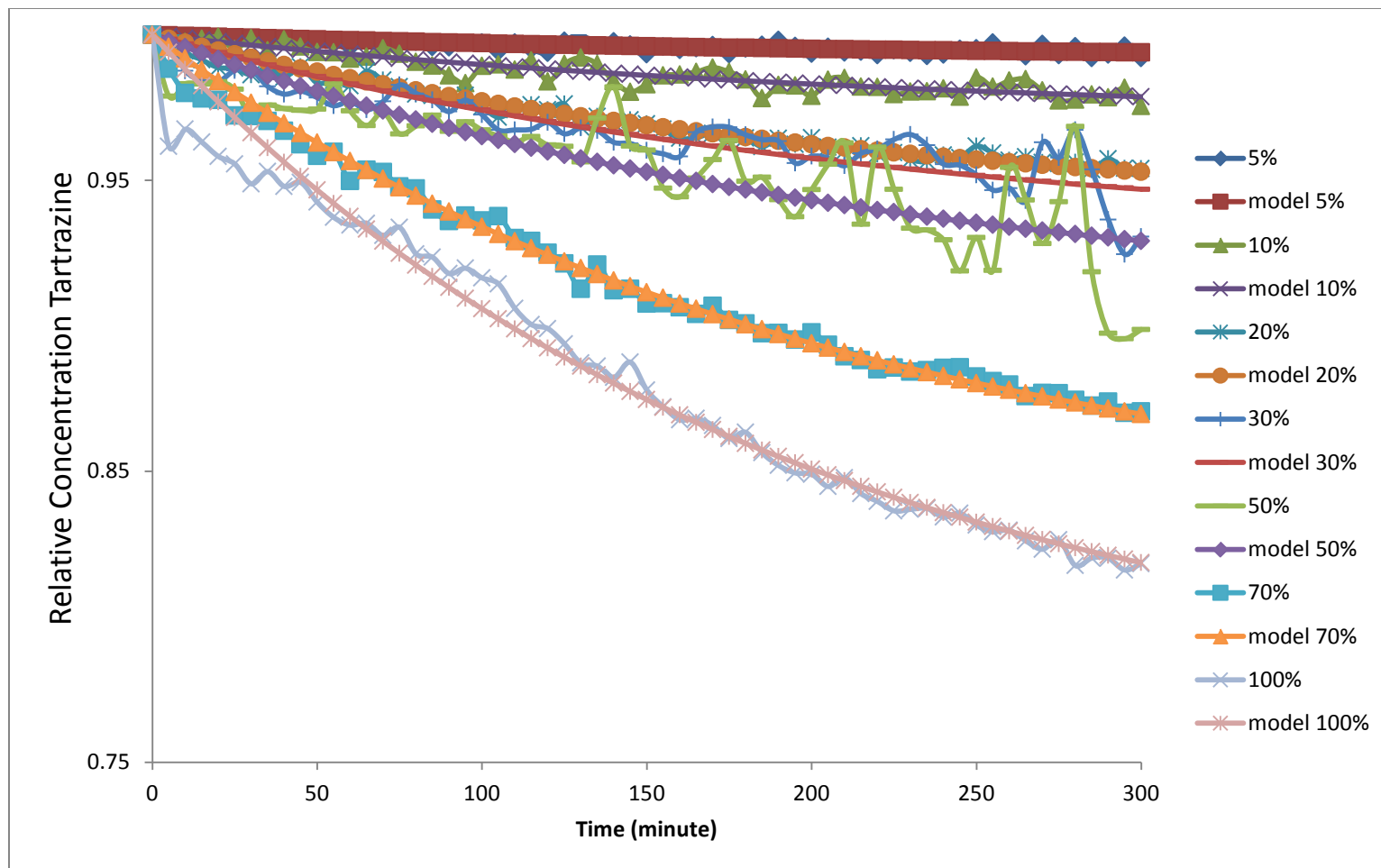


Figure 7 - Third trial relative concentration of tartrazine as function of time and duty cycles at 1.45 ml/min reactor rate.

Initial concentration (C_0) was approximately 0.05mol/L tartrazine and 0.005 mol hydrogen peroxide.

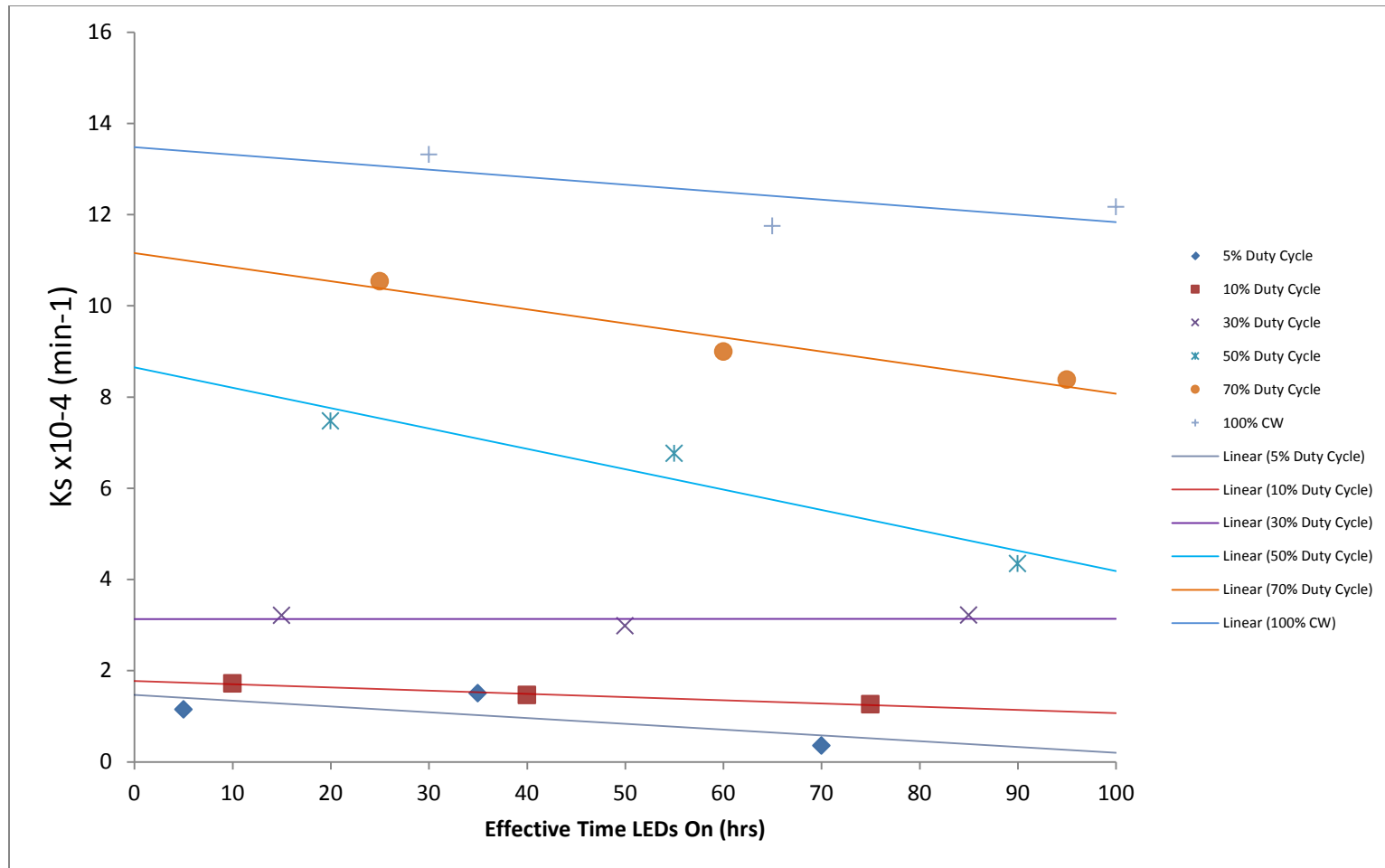


Figure 8 - Effect of time of use on LEDs apparent effectiveness

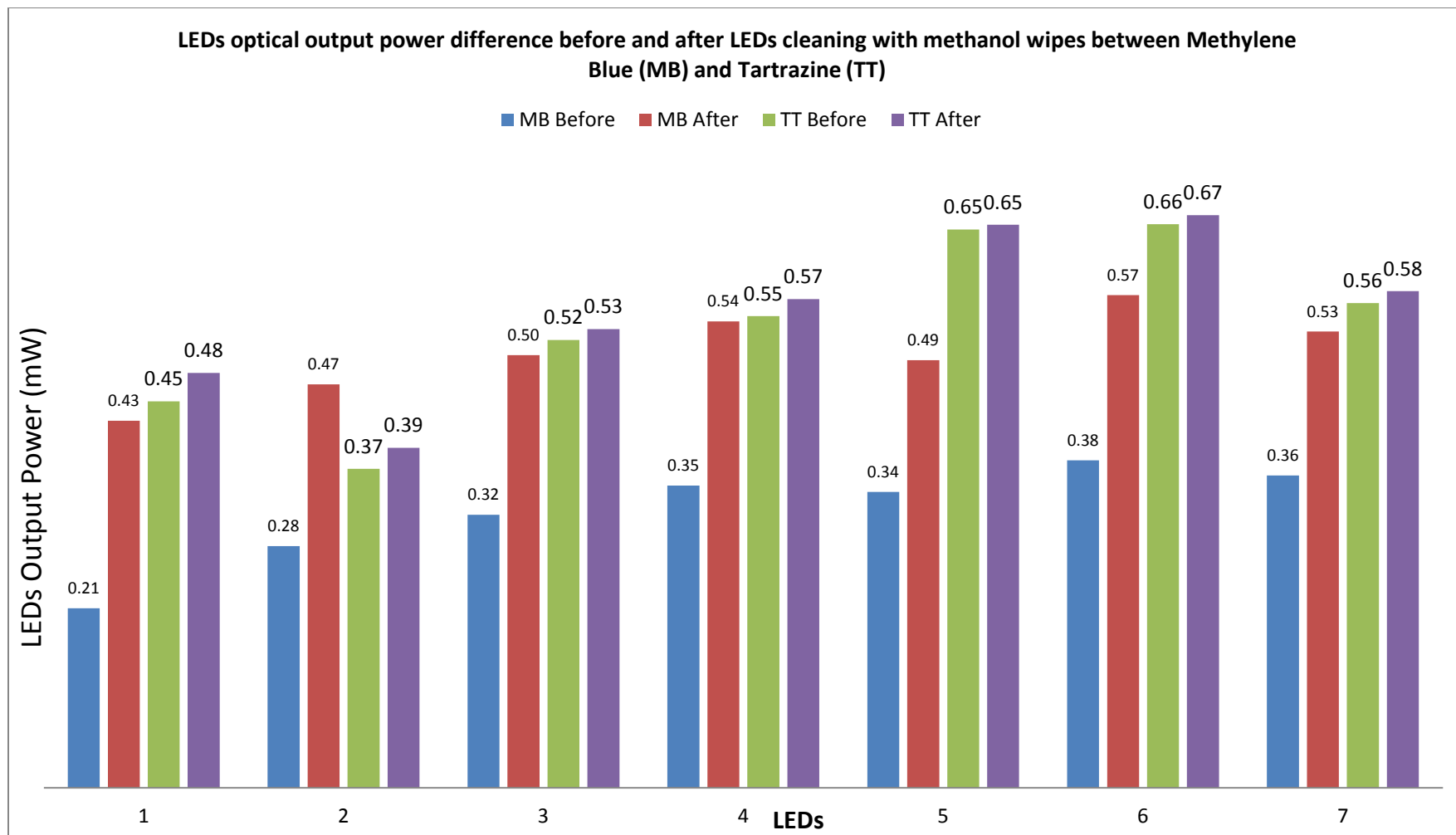


Figure 9 - Methylene Blue and tartrazine UV LEDs output power before and after cleaning with methanol wipes

Furthermore, at the end of the MB and TT third experiments, LEDs were measured, cleaned with methanol wipes, and then measured again. The results are shown in Figure 9, where LEDs optical output power before and after cleaning for both MB and TT is illustrated. The overall decline in TT/LEDs output power was less compared to that of MB/LEDs power output. For example, with LED #1, the output power for TT increased only by 7%, from 0.45 to 0.48 mW. In comparison, MB LED #1 had a 52% increase, from 0.21 to 0.43 mW. Note that the LEDs used in both MB and TT experiments were the same, and were positioned in the same place in the reactor. This small drop in output power was because tartrazine has a significantly smaller fouling effect on the quartz lenses of the LEDs. As seen in Figure 9, fouling was a major factor in the performance of a UV LED reactor for MB degradation. A future reactor design must incorporate a mechanism that will allow the operator to easily clean the LED's quartz lenses between trials in order to minimize the fouling effect.

The apparent rate constant increased proportionally with duty cycles. Figure 10 shows the average of three independent trials at each duty cycle. As shown, the rate constant increased linearly with duty cycles, and is consistent with Almquist's (2014) results. Note that the rate constant for MB was nearly 8 times greater than that of TT. For example, at 100% duty cycle, the rate for tartrazine destruction was only 0.0012/min, compared to 0.0083/min MB rate of destruction. This explains why tartrazine was partially removed during experiments. Tartrazine destruction accounted only for 19% during the first experiment compared to MB at nearly 80% removal (Almquist, 2014) when LEDs were 100% powered. The seemingly slow rate of destruction of tartrazine may be due to its chemical structure, which may be intrinsically resistant to oxidation.

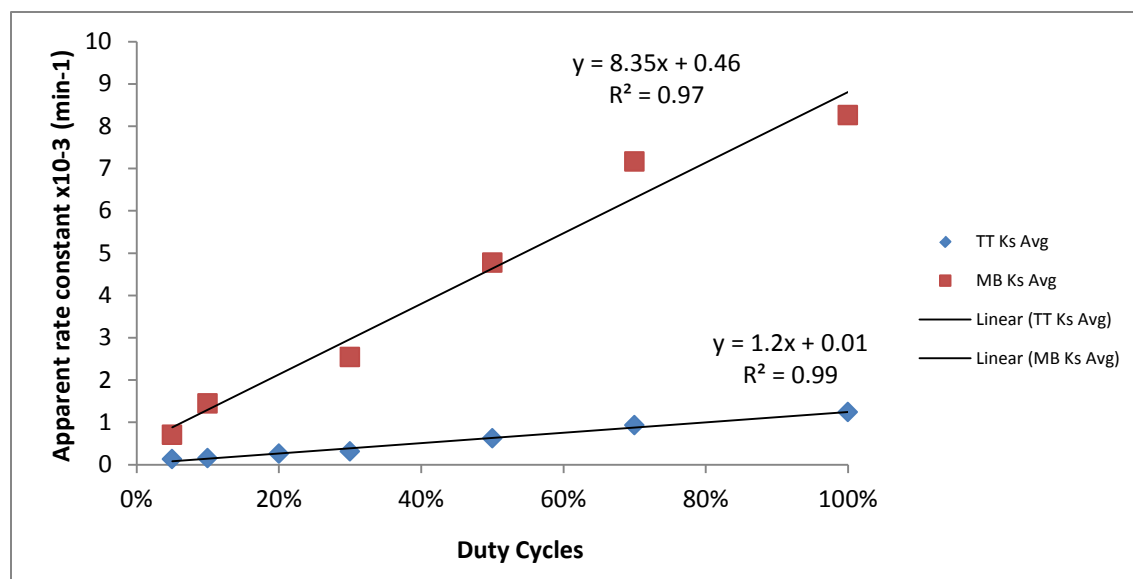


Figure 10 - Rate constant comparison between MB and TT as duty cycles increase

Another potential explanation is that scavengers may be generated. Alpert et al (2009) explained that scavengers, such as dissolved organic carbon, alkalinity, and chloramines, can consume substantial amounts of hydroxide radicals needed to destroy contaminants in the water matrix. Among the three radical scavengers, dissolved organic carbon has the most significant effect (Alpert et al, 2009). The reaction system describing oxidation of tartrazine by hydroxyl radical was not evaluated. Therefore, qualitative and quantitative data on the potential byproducts effects were not determined. Future research in this discipline needs to define the chemical reactions involved in the degradation of tartrazine and account for the factors that could have an impact in the performance of the UV/H₂O₂ reaction.

5.3 Data scatter investigation

Reoccurring data scatter in tartrazine experimental results was observed at mid-range duty cycles. This cyclic concentration pattern, seen as swirly lines about the models, was also observed in MB experimental results, and consistently occurred between 10% and 70% duty cycles. A proposed hypothesis suggested that data scatter was due to incomplete mixing in the UV reactor. A model constructed by Almquist et al (2014) using COMSOL, a multiphysics software package capable of computing fluid dynamics, showed that by increasing the velocity profiles in the reactor from 0.0122 to 0.1 m/s, the disturbance in fluid flow increased. The model suggested that data scatter increases as reactor flow increased, however no experiment was conducted to validate this hypothesis. Hence, the occurrence of this scatter data at specific duty cycles has yet to be explained. To investigate the effect of velocity profile and mixing in the reactor, two additional experiments were conducted, one at halved reactor flow, and another with a mechanically mixed reactor.

5.3.1. Halve Reactor flow effect on data scatter

The UV reactor flow was halved at 0.7 ml/min, and the result, depicted in Figure 5.8, shows an apparent improvement in the cyclic patterns at 30% and 50% duty cycles. A best-fit linear regression line was drawn to determine the values of R^2 for each trial. The linear regression lines minimize the sum-of-squares of data scatter vertical distances and assign a R^2 value between 0.0 and 1.0, such that when that value approaches 1.0, the reduction in data scatter can be determined. At 0.7 ml/min flow, R^2 values for 30% and 50% duty cycles were 0.95 and 0.98 respectively; this is an improvement from 0.80 at 30% duty cycles and 0.73 at 50% duty cycles when the reactor flow was 1.45 ml/min. However, at lower duty cycles, R^2 values decrease. For example, at 10% and 20% duty cycles, R^2 values were 0.81 and 0.93 at 1.45 ml/l reactor flow respectively, compare to 0.80 and 0.82 at 0.7 ml/l reactor flow. This suggests that the UV reactor was not mixing properly. UV dose is not being distributed equally inside the reactor, leaving pockets of poorly degraded tartrazine particles in the solution.

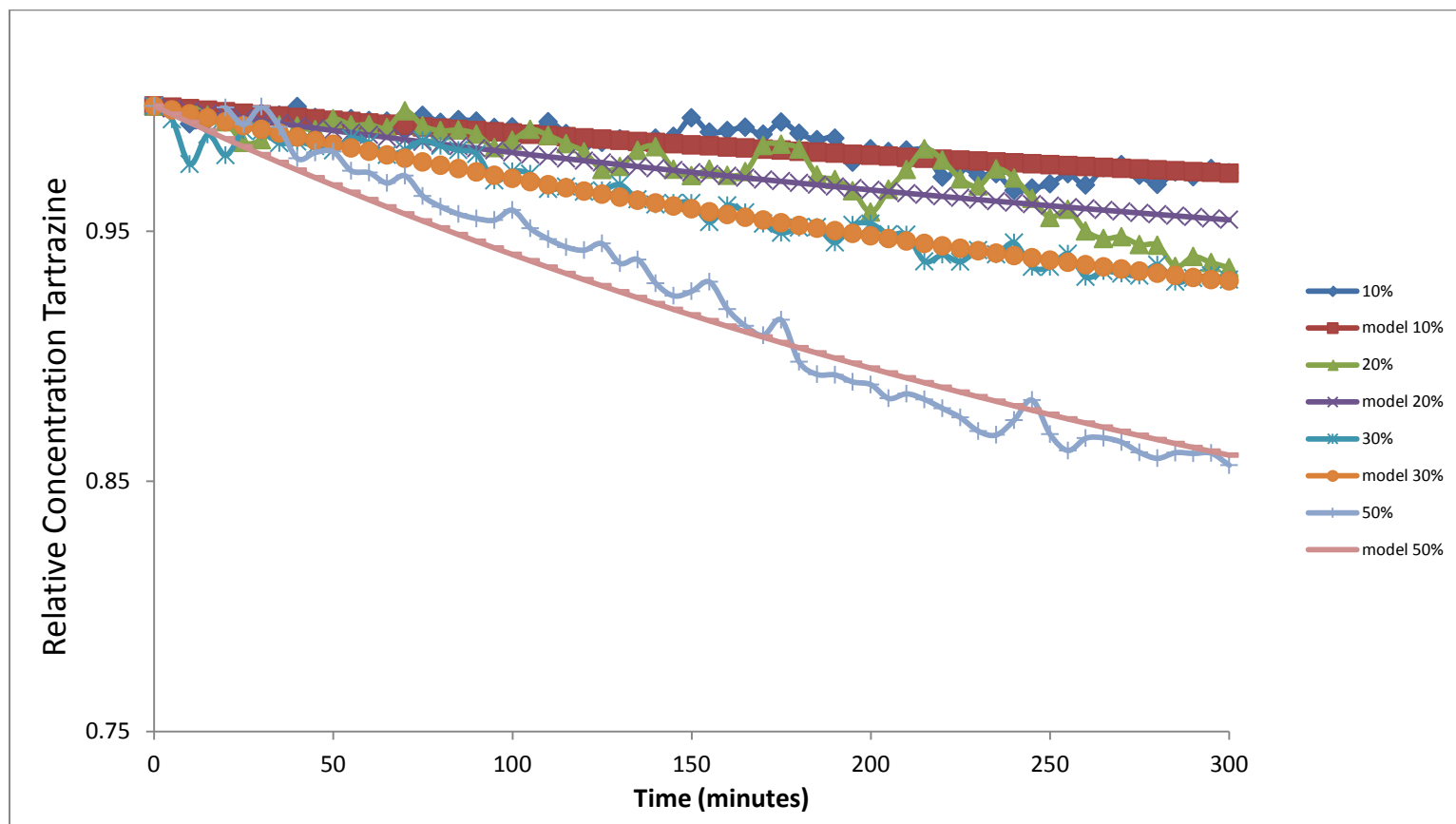


Figure 11 - Fourth experiment: relative concentration of tartrazine as function of time and duty cycles at 0.7 ml/min reactor rate. Initial concentration (C_0) was approximately 0.05mol/L tartrazine and 5mol/L hydrogen peroxide.

Alpert et al., (2009) noted that a multiple-lamp reactor has several limitations, like reflection, refraction, shadowing, and lamp characteristics, which could impact the distribution irradiance rate within the reactor. Fluid particles moving inside a multiple-lamp reactor will travel different trajectory, and the total irradiance power received per each fluid particle will vary with distance to these LEDs and the absorption characteristics of the solution.

Duty cycle, described by the frequency (pulsing) at which UV LEDs power is on and off, contributes to this cyclic pattern. Such that, each time UV LEDs are pulsed, they irradiate pockets of fluid particles, which in turn move disorderly from their trajectory due to reactor turbulence, resulting in several pockets of unmixed fluid particles moving randomly inside the reactor. Jenny et al, (2014) observed that when there is an increase in flow, the mixing intensity also increases. As a consequence, particles exiting the reactor outlet will have a different degree of irradiance dose, and the intensity of this irradiance dose is dependent upon the exposure length of the fluid particles to the LEDs pulsed energy. Hence, the probability that these randomly moving particles are exposed to the UV irradiance increases with duty cycles and with lower reactor flow; because at lower reactor flow, the resident time increases and more particles are exposed to UV dose. At halved reactor flow and low duty cycles, the slowly moving fluid particles are lesser probable to be equally exposed to the UV dose, as the frequency at which the UV LEDs power are on decreases. This is a potential explanation for increased data scatter at halve reactor flow for lower duty cycles. Reducing reactor rate improve data scatter for higher duty cycles, but worsen the scatter for lower duty cycles as a result of incomplete reactor mixing.

5.3.2. Effect of stirred reactor on data scatter

The second test was conducted to evaluate the effect of mechanically mixed UV reactor on the performance of the LEDs. A two-inch magnet was inserted inside the UV reactor, and the reactor was placed on a Corning Stirrer, Figure 12, to allow mechanical mixing. The UV reactor was inverted such that LEDs were facing downward toward the stirrer. The UV reactor flow was maintained at 1.45 ml/min during six experimental trials at 5%, 20%, 30%, 50%, 70%, and 100% duty cycles.



Figure 12 - Mechanically mixed UV reactor with Corning Stirrer

The result for the stirred reactor, in Figure 13, shows an apparent improvement in the variability of data scatter at each trial. The values of R^2 have significantly improved from a 0.57- 0.96 range for non-stirred reactor to 0.70 - 0.99 range for stirred reactor, a

23% improvement at 5% duty cycles, and a 3% at 100% duty cycle. These results further indicate that non-stirred reactor partially mix dye solution, and contributes to the data scatter observed throughout these experiments. Additionally, stirred reactor moderately improved the degradation of tartrazine for some duty cycles as shown in Figure 14. For instance, at 100% duty cycle, approximately 23% of the dye was degraded when the reactor was mechanically stirred, compared to 19% degradation when the reactor was not stirred; at 50% duty cycle, 14% degradation for stirred reactor, compared to 10% for non-stirred reactor. The apparent first order rate constant (k_s) for stirred reactor also increases linearly with duty cycles, and appeared to have slightly improved over the non-stirred reactor rate constant. The adjusted rate constants (k_{adj}) values for the stirred and non-stirred reactor are shown in Figure 15. The rate constant was adjusted to the duty cycles by dividing k_s by the duty cycle. For the non-stirred reactor, k_{adj} is significantly larger at 5% duty cycle than for the higher duty cycle conditions. The k_{adj} value at 5% duty cycle is 200% larger than the average of the other higher duty cycles. However, the k_{adj} values for the stirred reactor showed small variance, and a potential indication that CSTR reactor may not offer expected gains observed in previous results at lower duty cycles. The values of k_{adj} for CSTR reactor at 50% and 70% duty cycles may be within the margin of error (5%). Though, this latest CSTR experiment was performed only once, more trials may be required to validate these results.

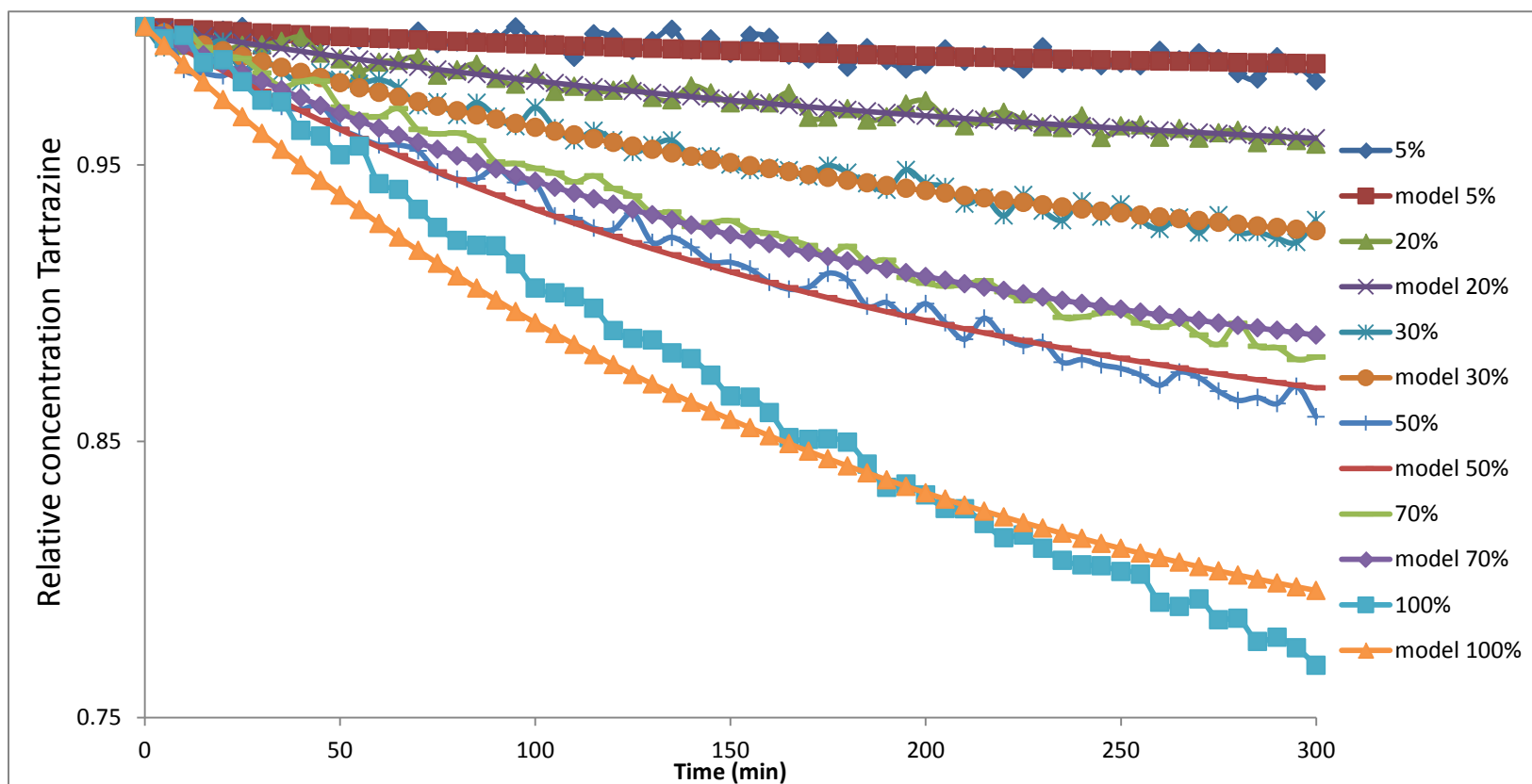


Figure 13 - Fifth experiment: relative concentration of tartrazine as function of time and duty cycles for a completely mixed reactor at 1.45 ml/min rate. Initial concentration (C_0) was approximately 0.05mol/L tartrazine and 5 mol/L hydrogen peroxide

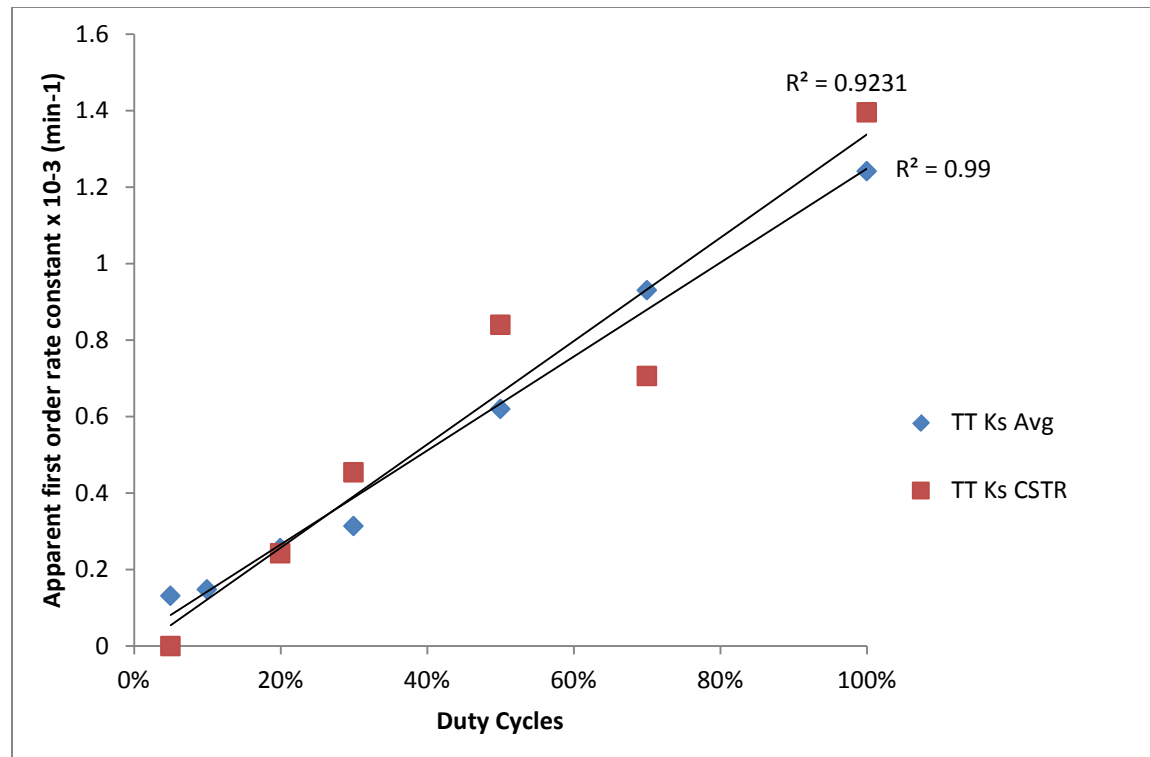


Figure 14 - First order rate constant between stirred and non-stirred reactor

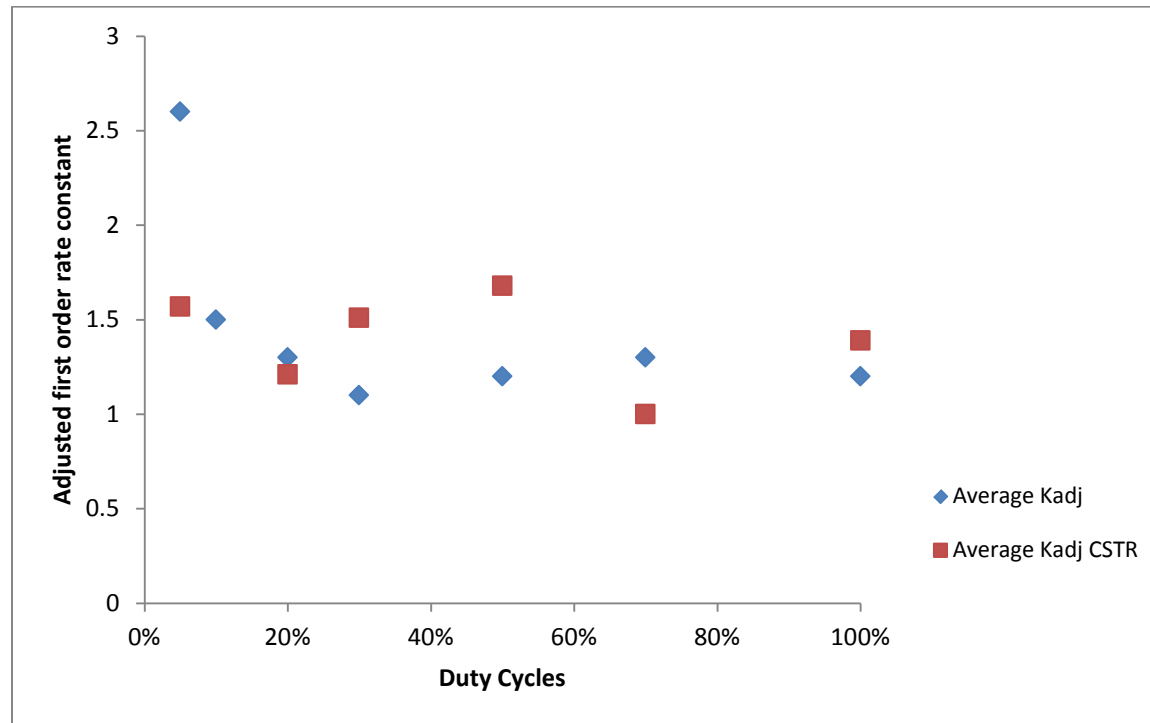


Figure 15 - Kadj values between stirred and non-stirred reactor

VI. Summary

This study investigated the advanced oxidation of tartrazine for continuous and pulsed UV LED reactor operating mode. The UV LED reactor was tested at seven duty cycles modes: 5%, 10%, 20%, 30%, 50%, 70%, and 100%. The degradation of tartrazine increased proportionally with duty cycles with maximum degradation at continuous mode (100% duty cycle). The rate of tartrazine degradation increased linearly with duty cycles. A cyclic pattern was observed at mid-range duty cycles in the experimental results for non-stirred reactor. The multiple-LED reactor used, as observed by Alpert et al., (2009), has design limitations which has caused pockets of unmixed fluid particles and has contributed to the data scatter observed in the experimental results. The UV reactor was later mechanically mixed and data scatter was significantly reduced. The degradation of tartrazine and its corresponding rate constant for the stirred reactor slightly improved over the non-stirred reactor. The values of the adjust rate constant k_{adj} for the stirred reactor showed limited variance across all duty cycles compared to the non-stirred reactor, where, at 5% duty cycle, the gain was 200% larger than the higher duty cycles. Tartrazine was selected for its anionic form to prevent film formation on the LED anionic silica glass surface, which can reduce the UV LED output power. The power loss after the experiment was negligible compared to the output power lost during MB experiment.

VII. Conclusion

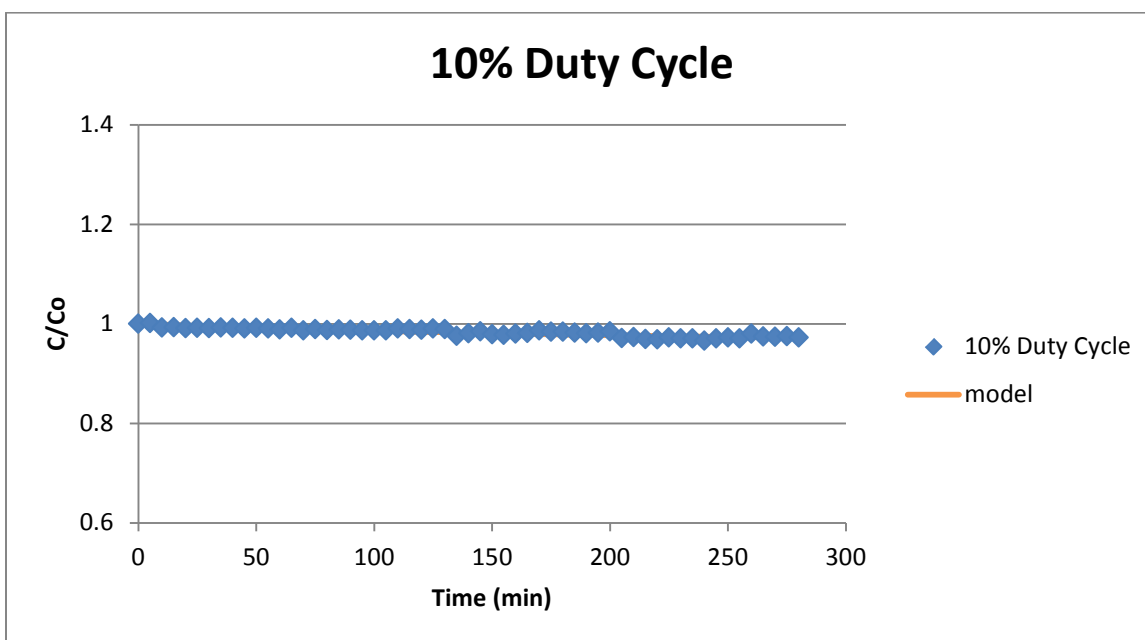
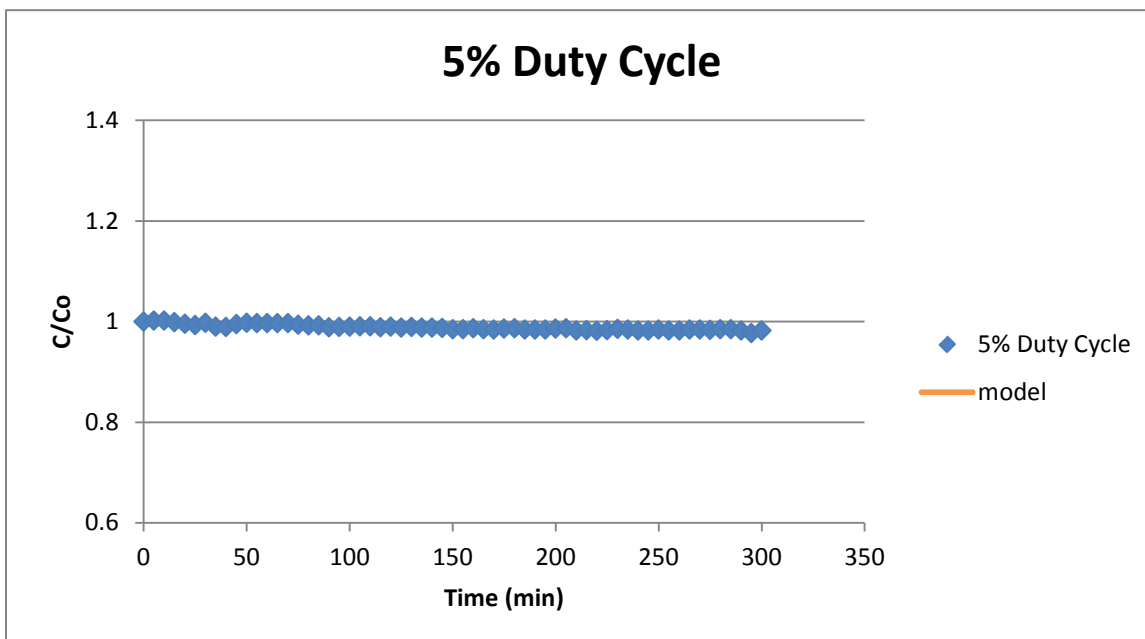
- Pulsed UV LED in an UV/H₂O₂ AOP can be used as water pretreatment method in the degradation of recalcitrant organic contaminants like tartrazine as shown in this research.
- The degradation rate constant of tartrazine increases linearly as duty cycles increase, and the maximum degradation was reached at continuous operating mode as expected.
- The observed data scatter in the experimental results is an indication that the UV reactor was not operating as a CSTR as assumed.
- Stirred reactor significantly decreases data scatter. R² improved from 0.57- 0.96 range for non-stirred reactor to 0.70 - 0.99 range for stirred reactor.
- The performance of UV LED reactor slightly improves when reactor is stirred.
- Tartrazine is not adsorbed on the LED glass window due to its anionic form, therefore the output power loss during the experiment was negligible.
- The adjusted rate constant k_{adj} value was 200% efficiency higher at 5% duty cycle than other higher duty cycles for non-stirred reactor. However, for stirred reactor, k_{adj} values for all duty cycles show very small variance.

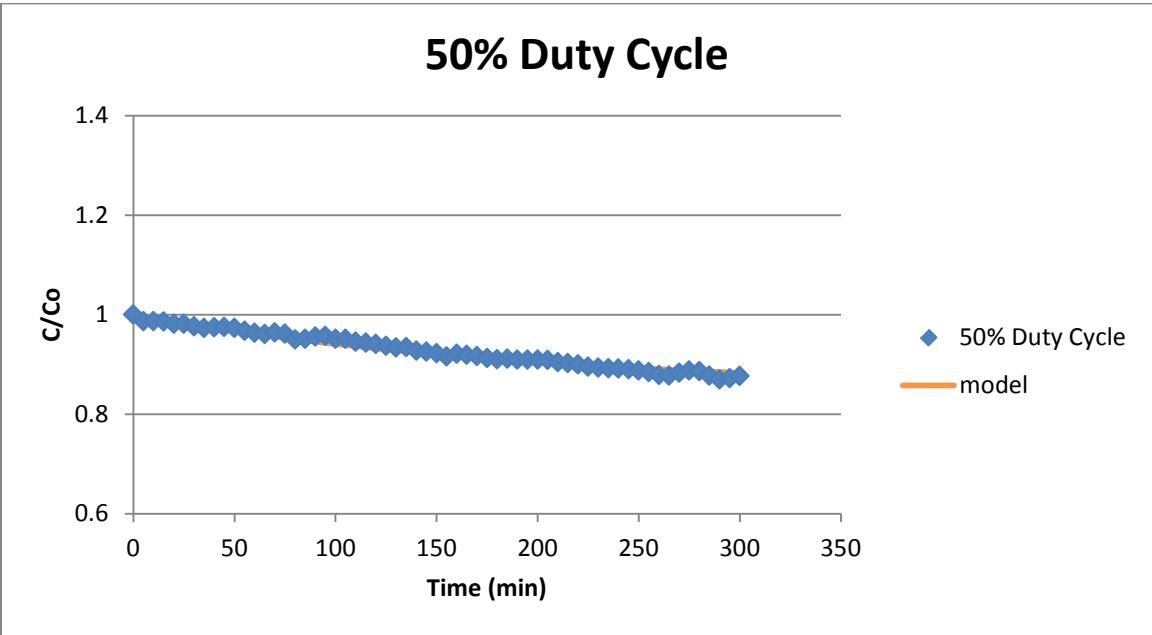
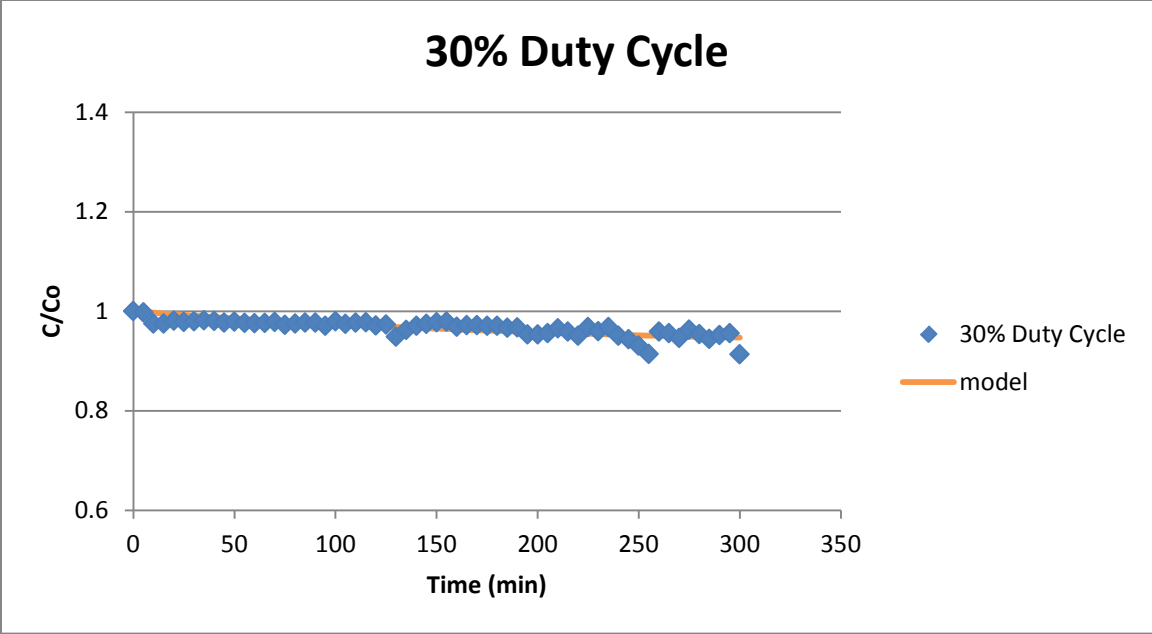
VIII. Future Work

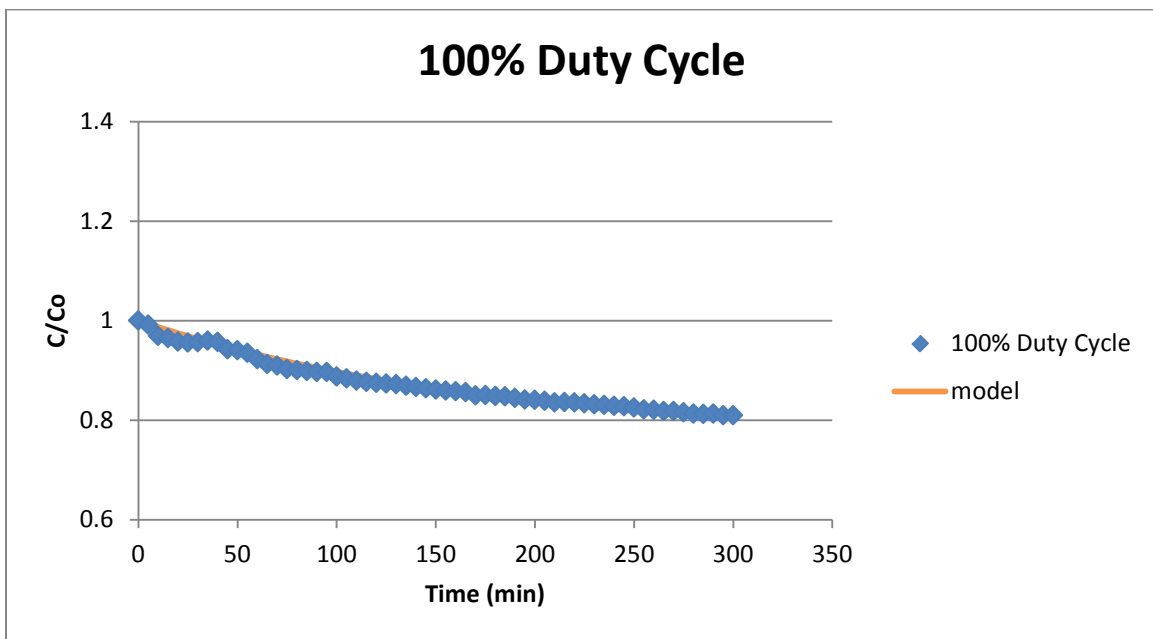
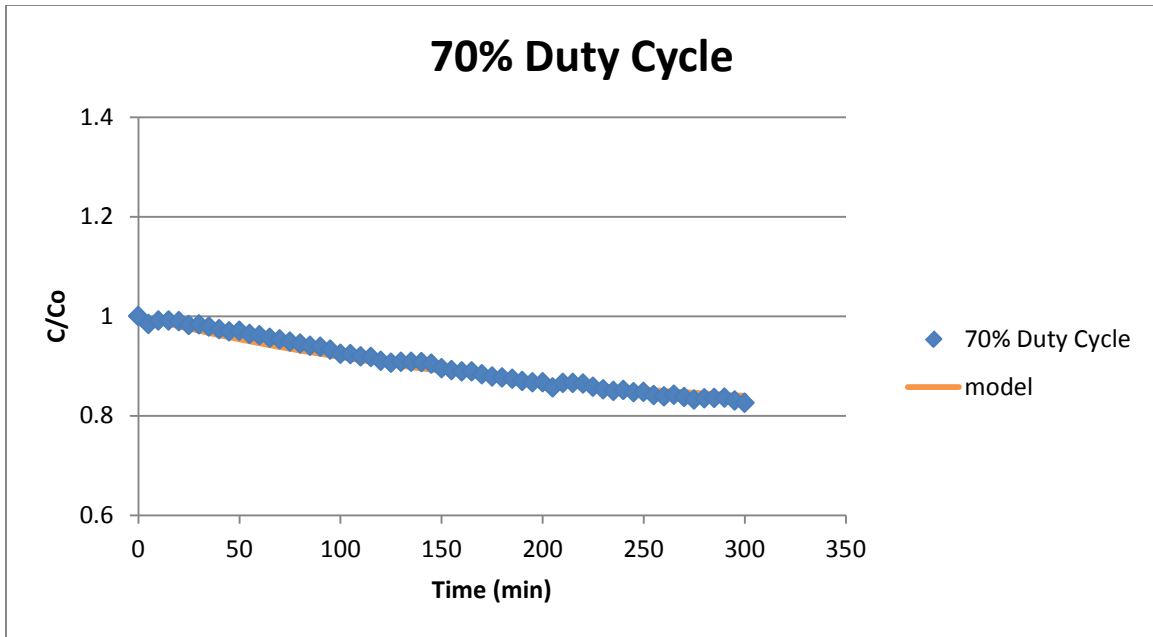
This research has shown that tartrazine dye can be degraded using AOP with a UV LED reactor. Nevertheless, further research is needed to address remaining questions regarding the characteristics of the UV LED reactor and to maximize the oxidation of tartrazine. Future work needs to:

1. Incorporate mechanical mixing in the reactor and conduct further experiments at lower duty cycles to evaluate the values of the adjusted K_s
2. Evaluate the effect of potential byproducts such as COT that may affect tartrazine degradation.

**Appendix A. Raw Data for First experiment AOP for Tartrazine/H₂O₂ with UV
LED**

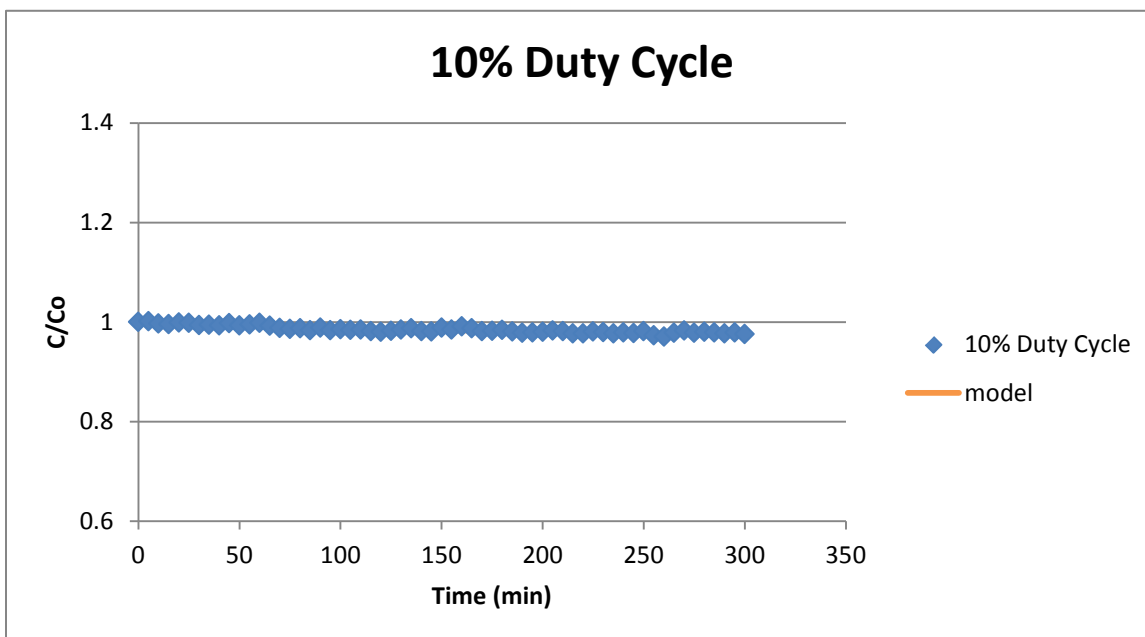
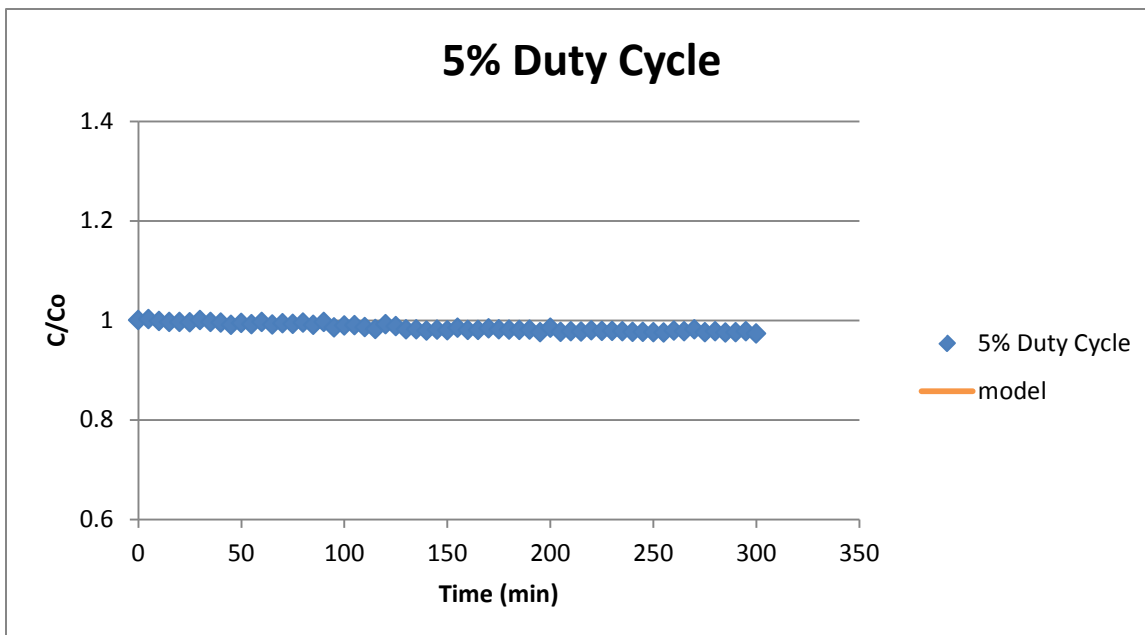


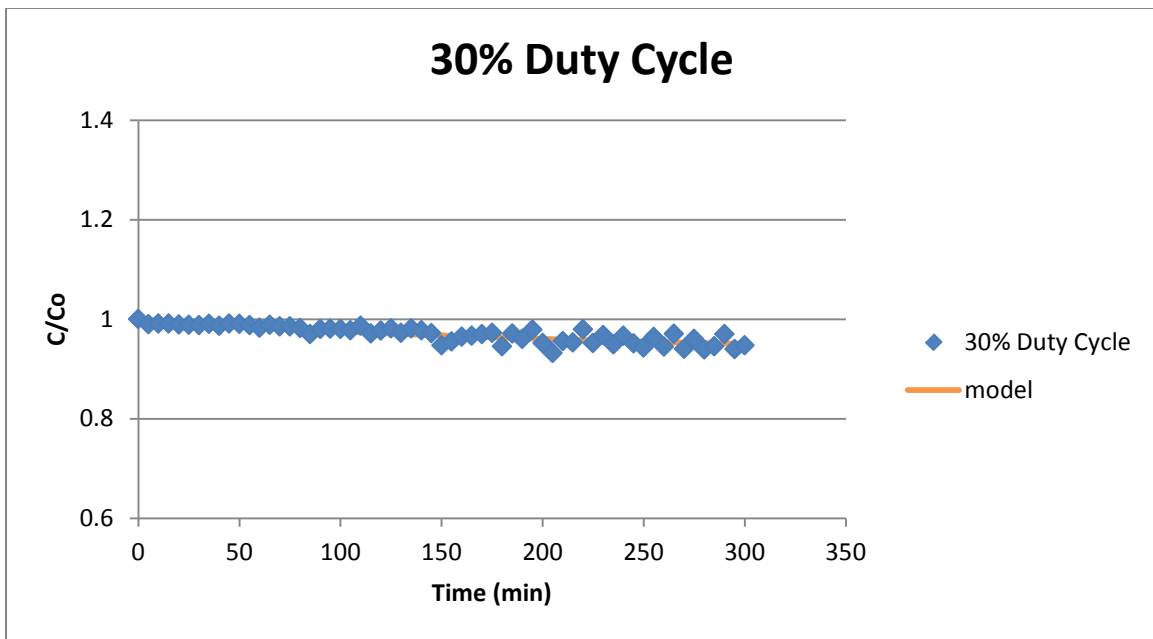
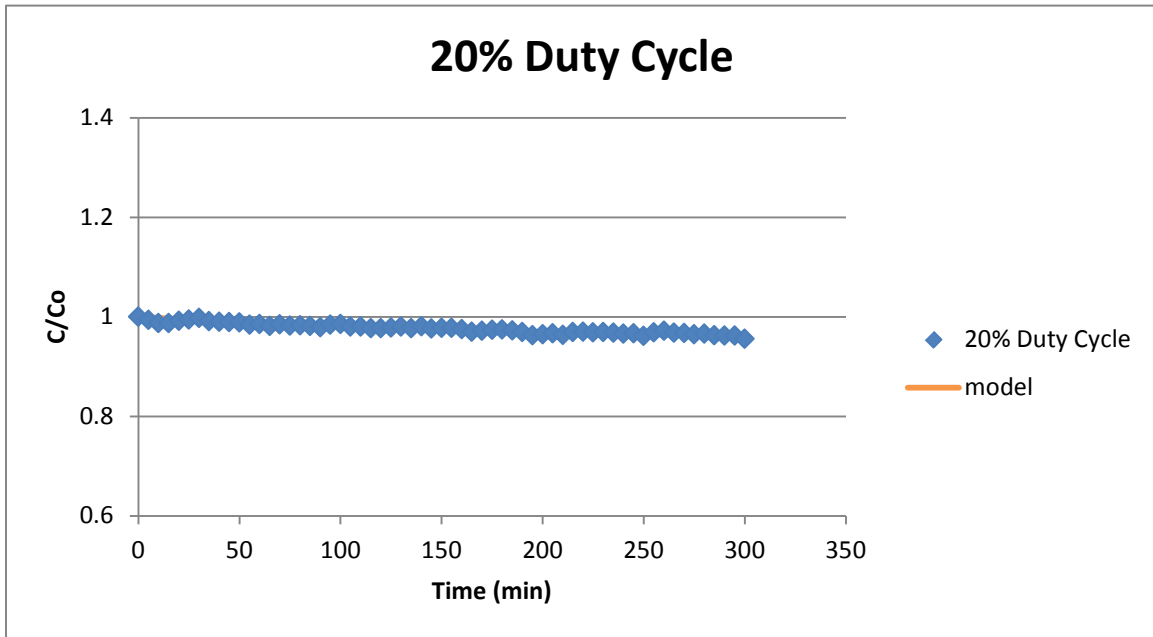


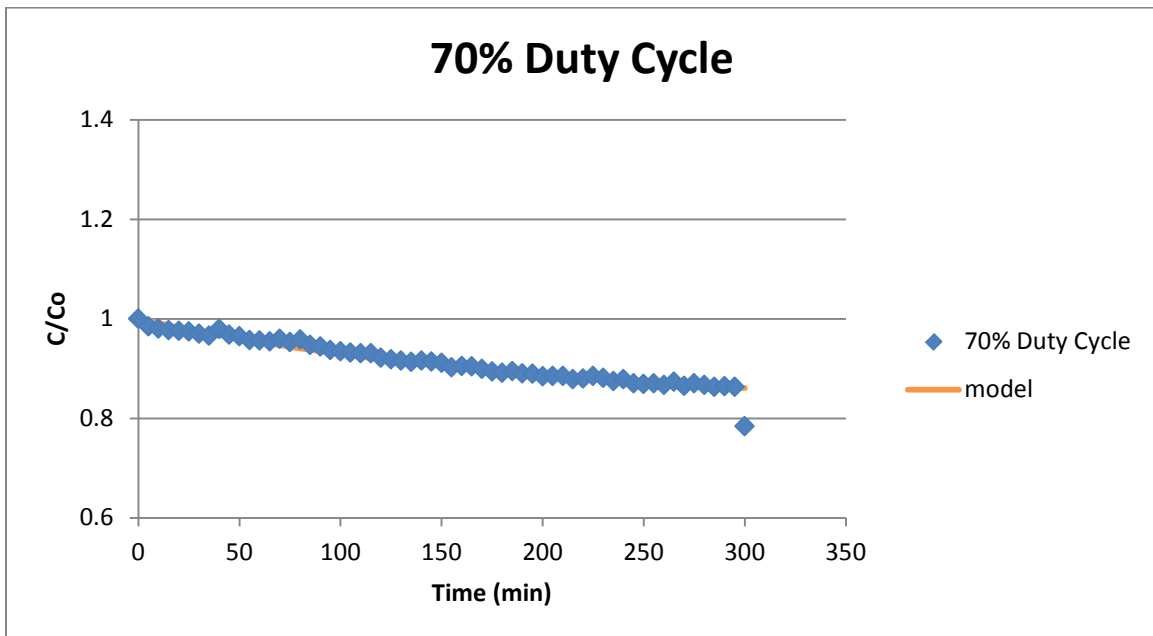
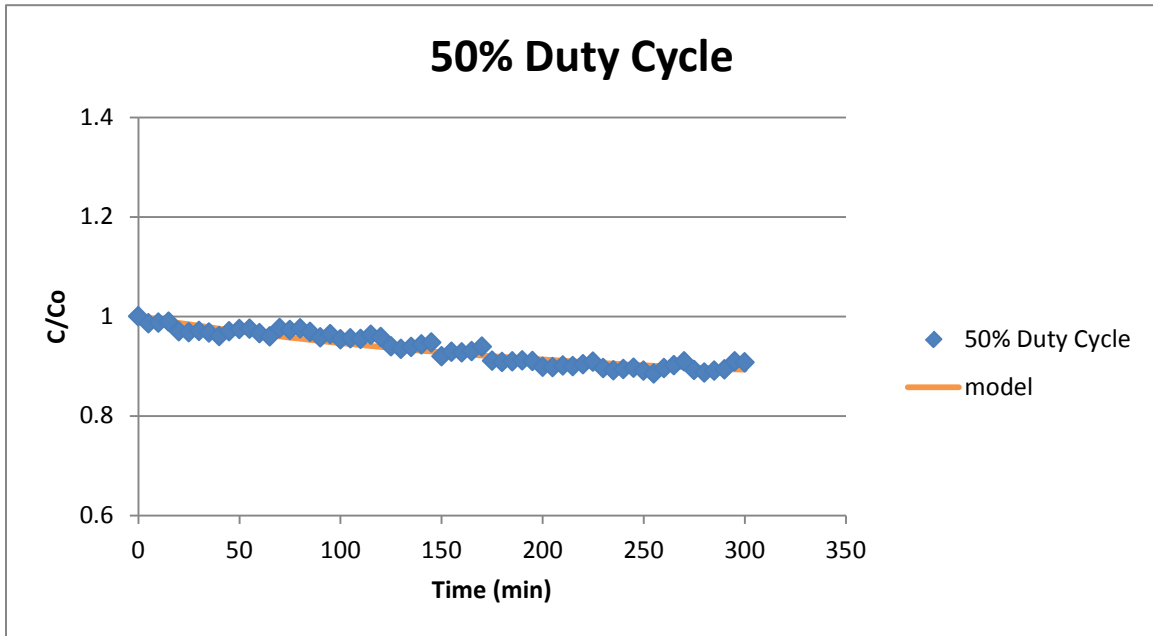


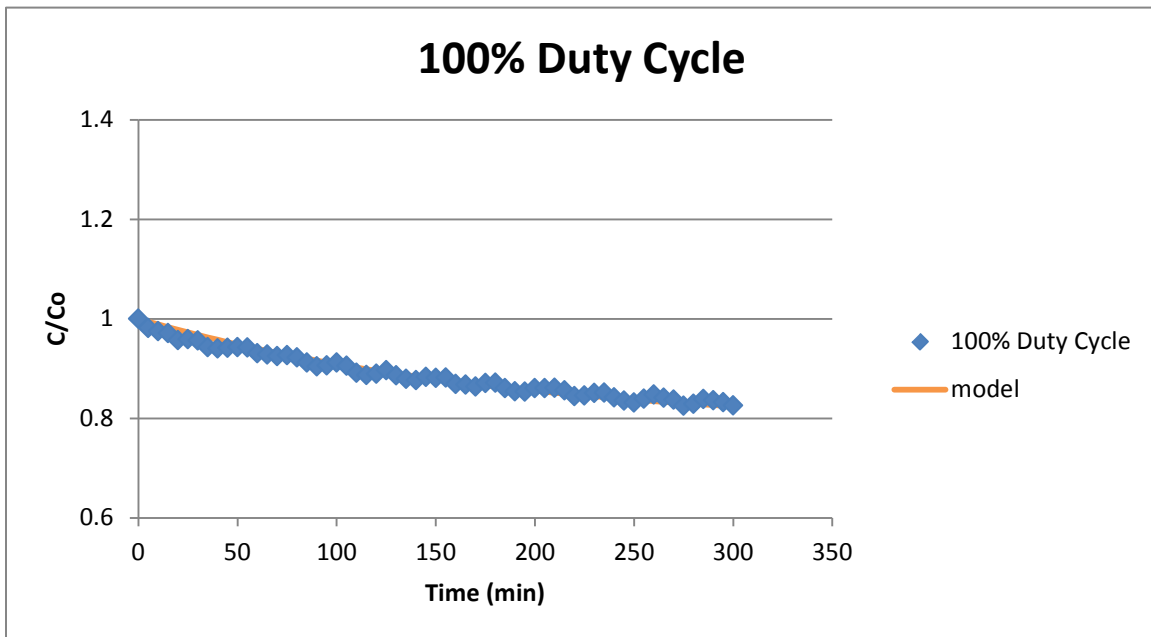
Appendix B. Raw Data for second experiment AOP for Tartrazine/H₂O₂ with UV

LEDs

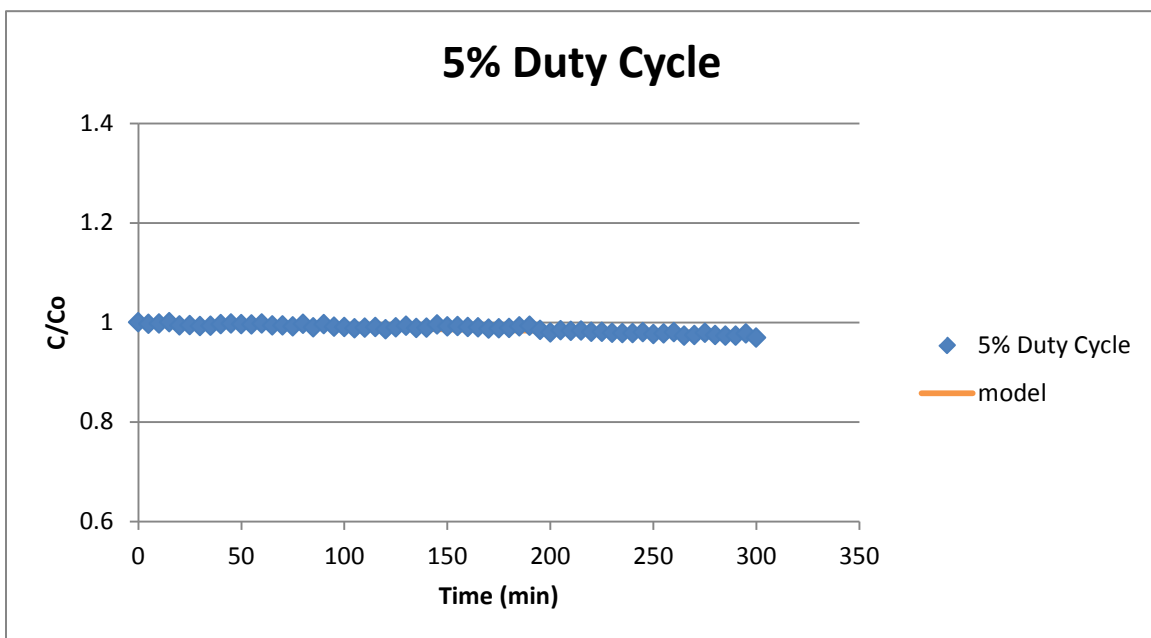


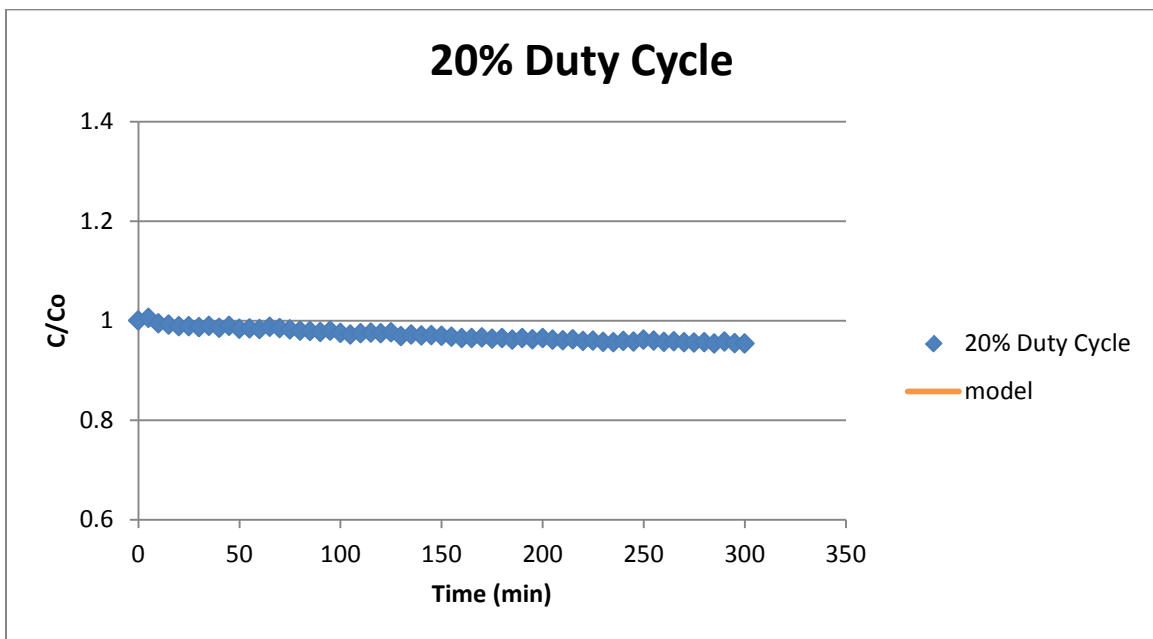
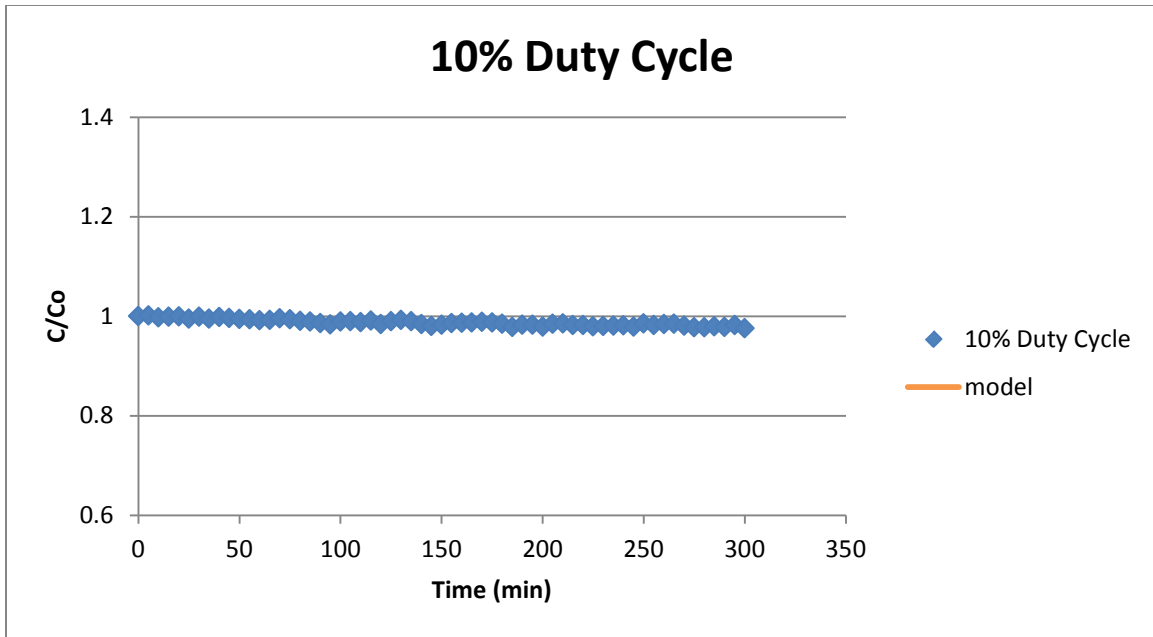


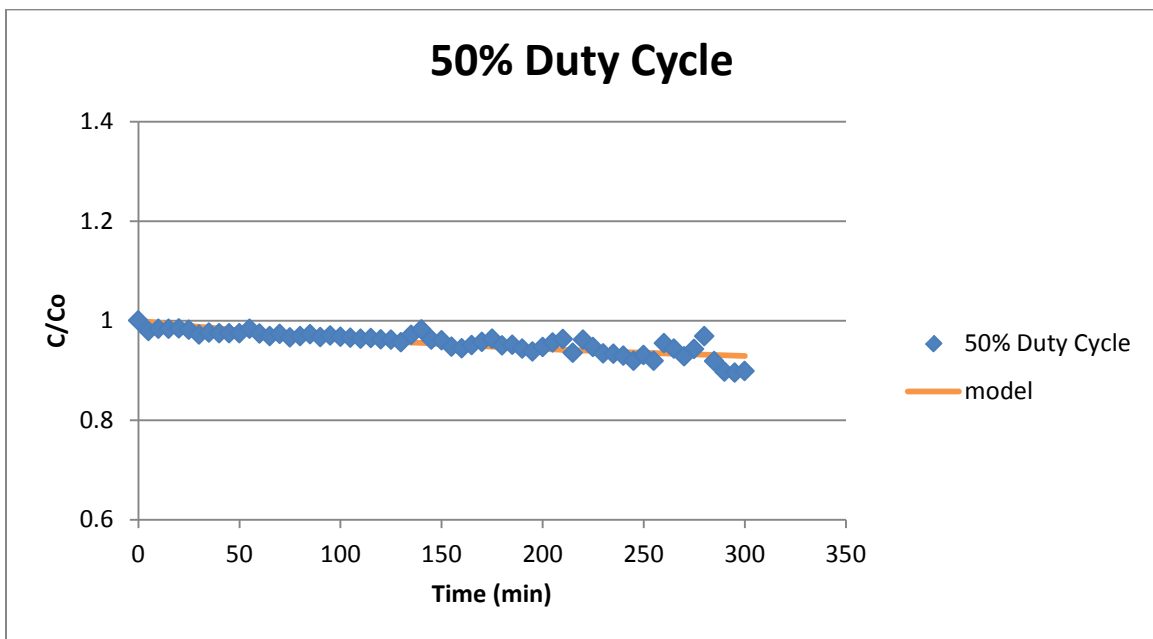
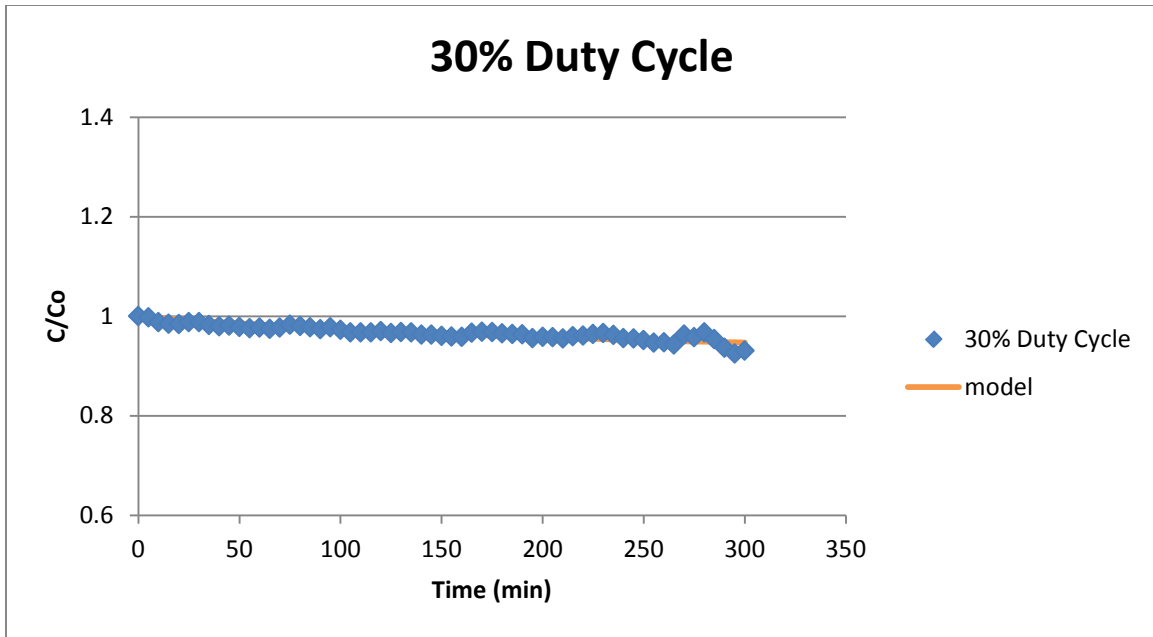


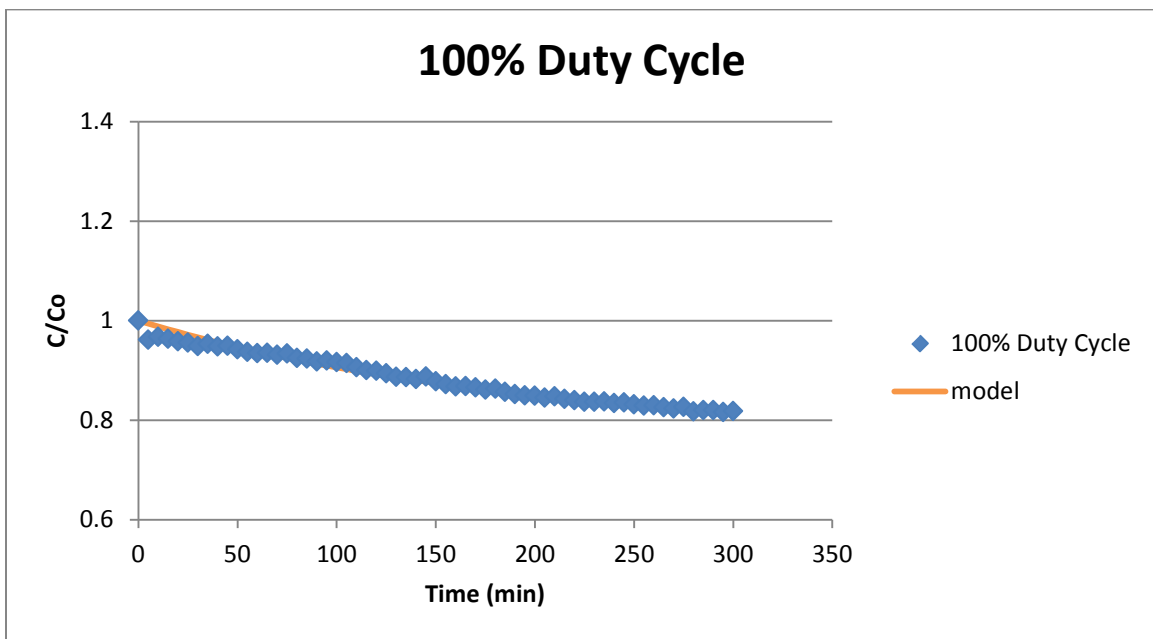
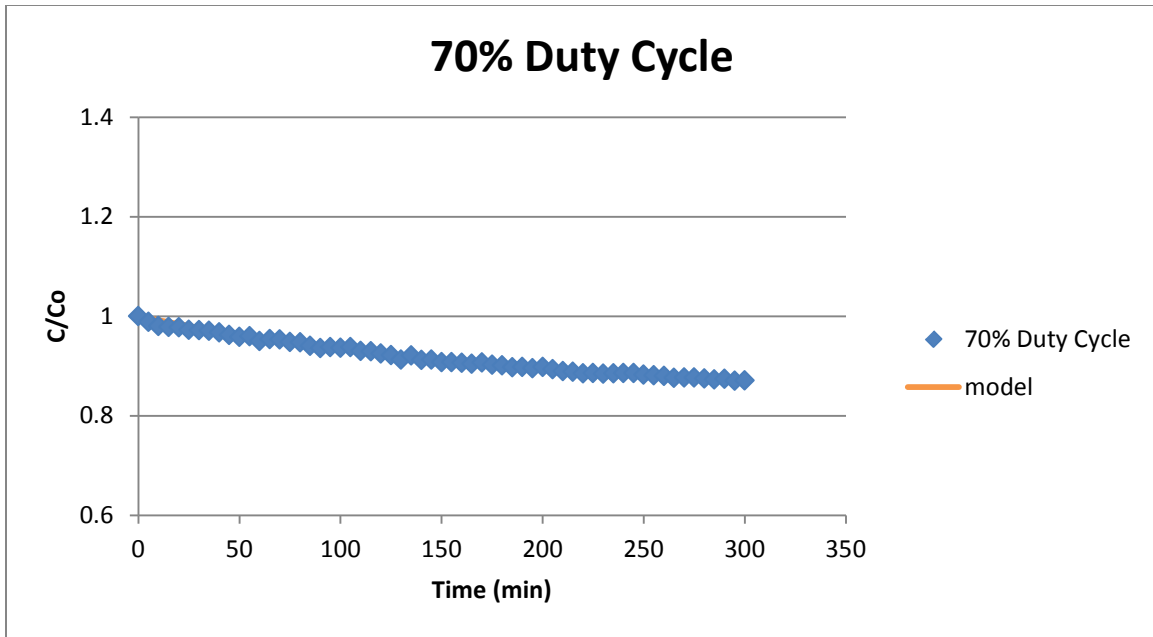


Appendix C. Raw Data for second experiment AOP for Tartrazine/H₂O₂ with UV LEDs

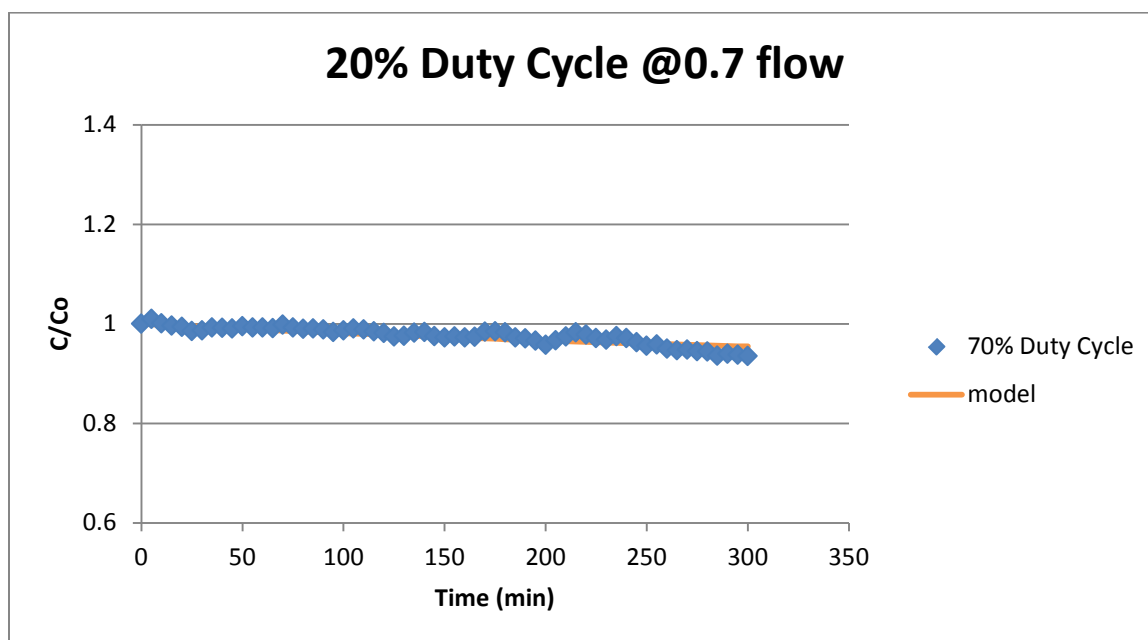
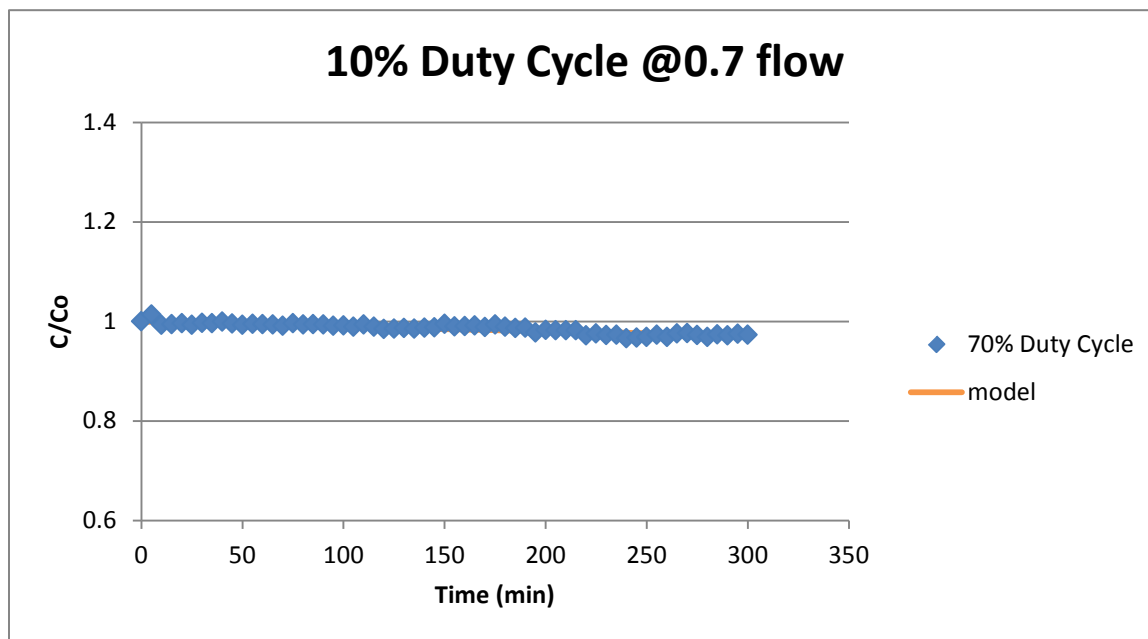


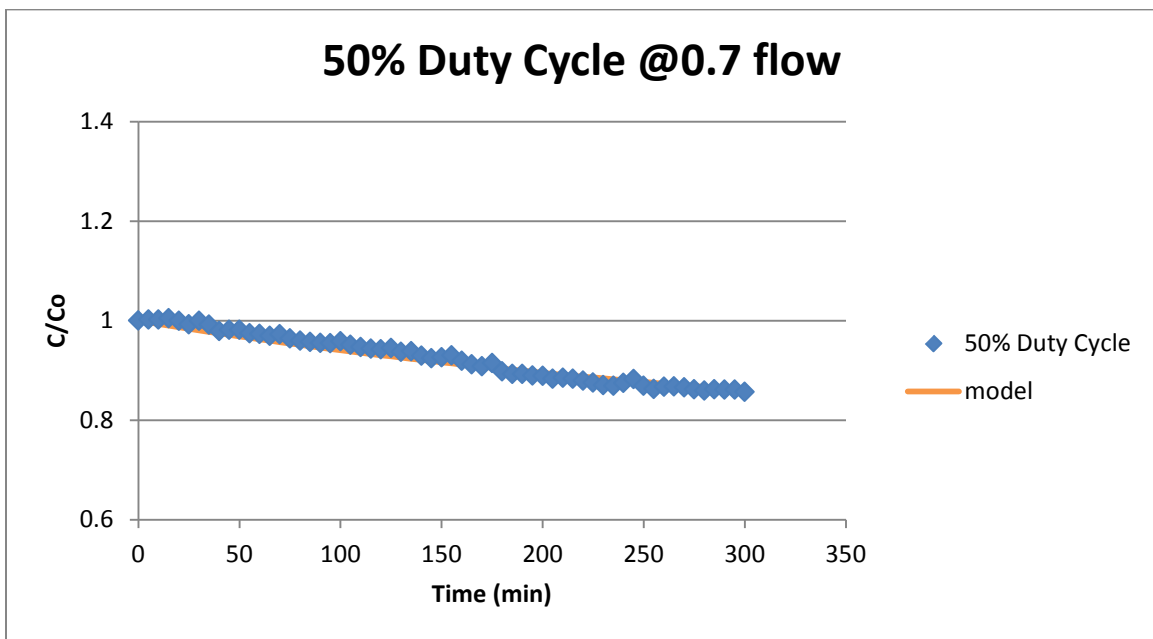
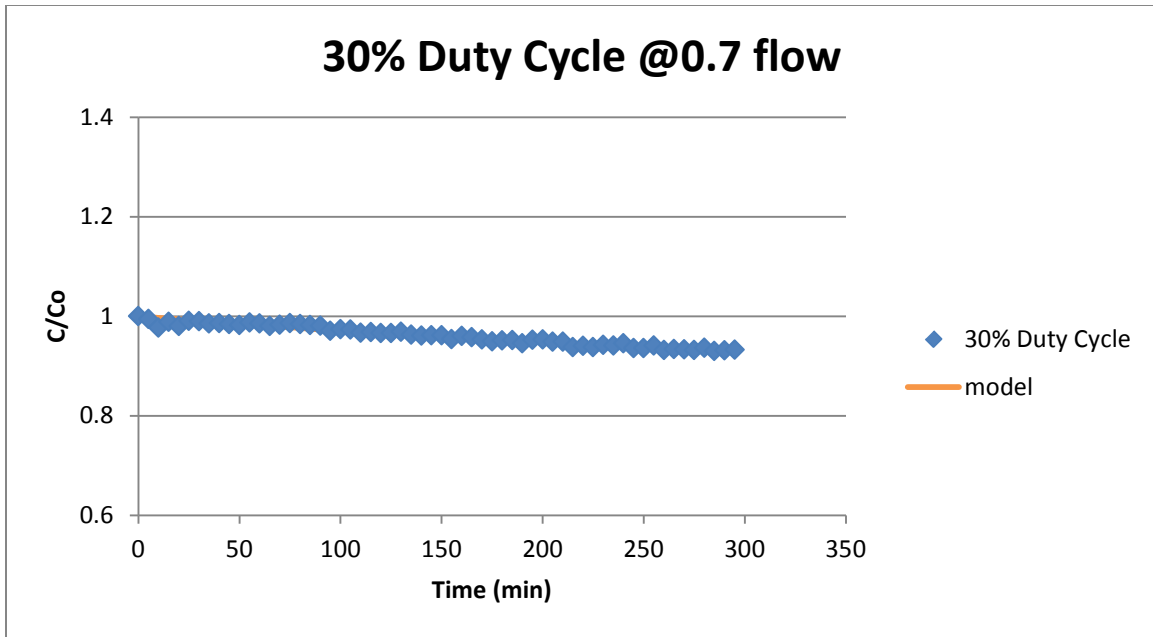




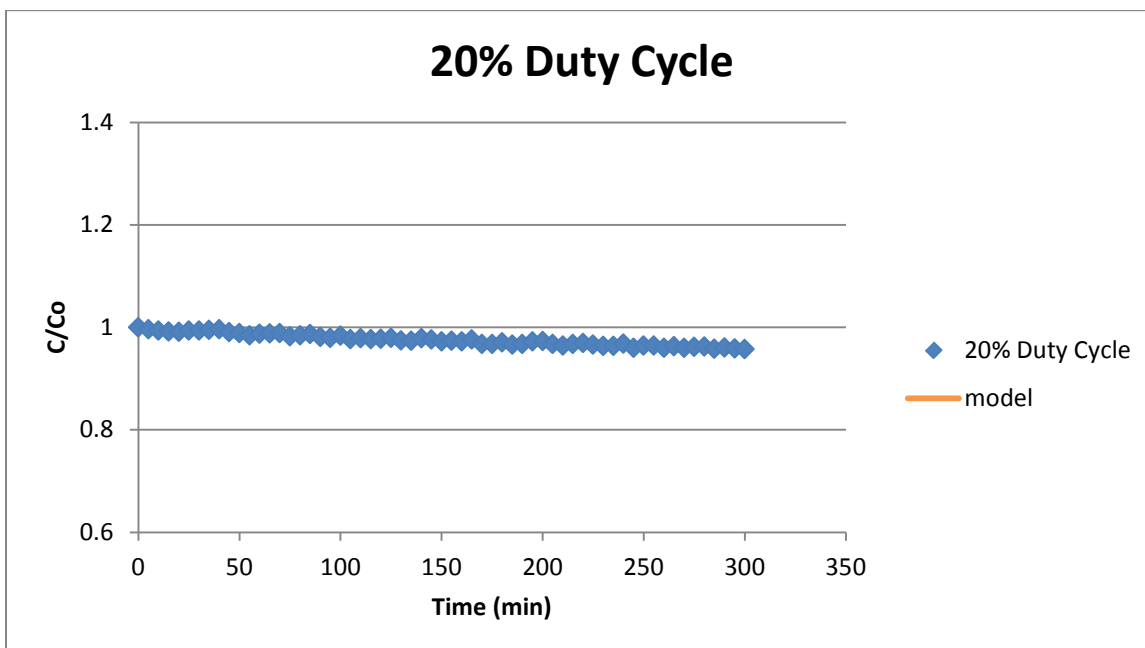
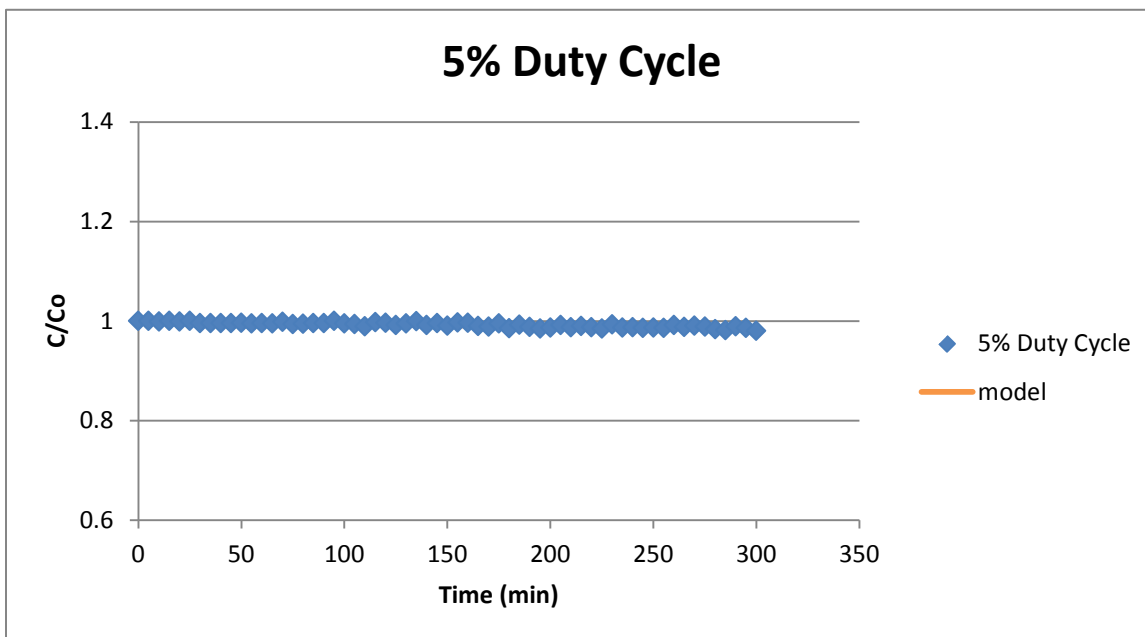


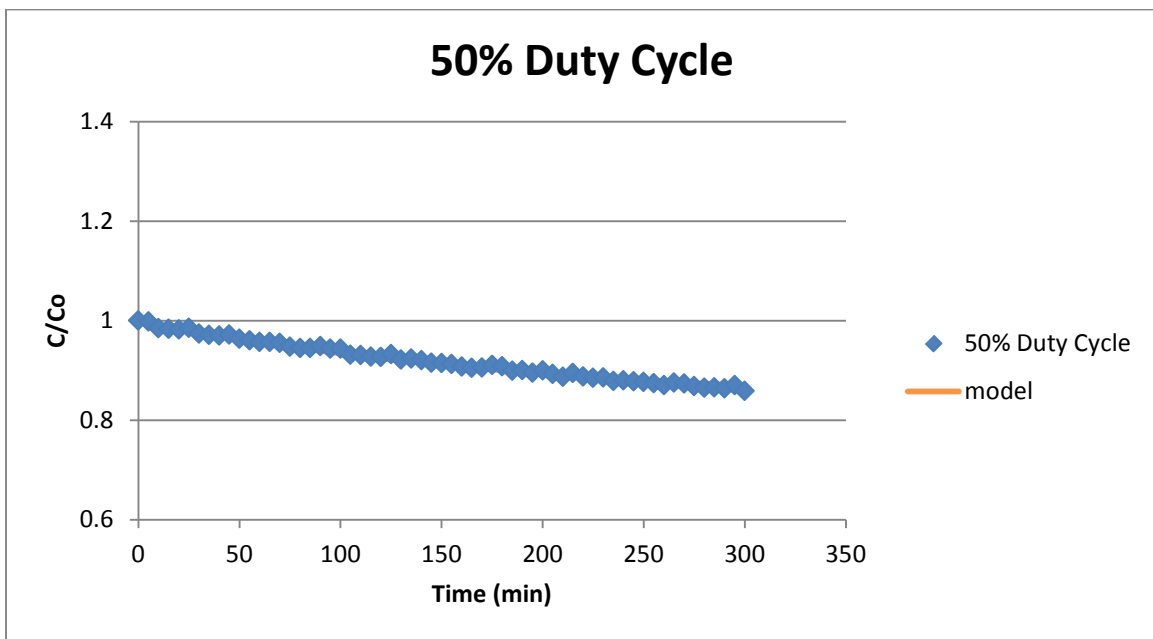
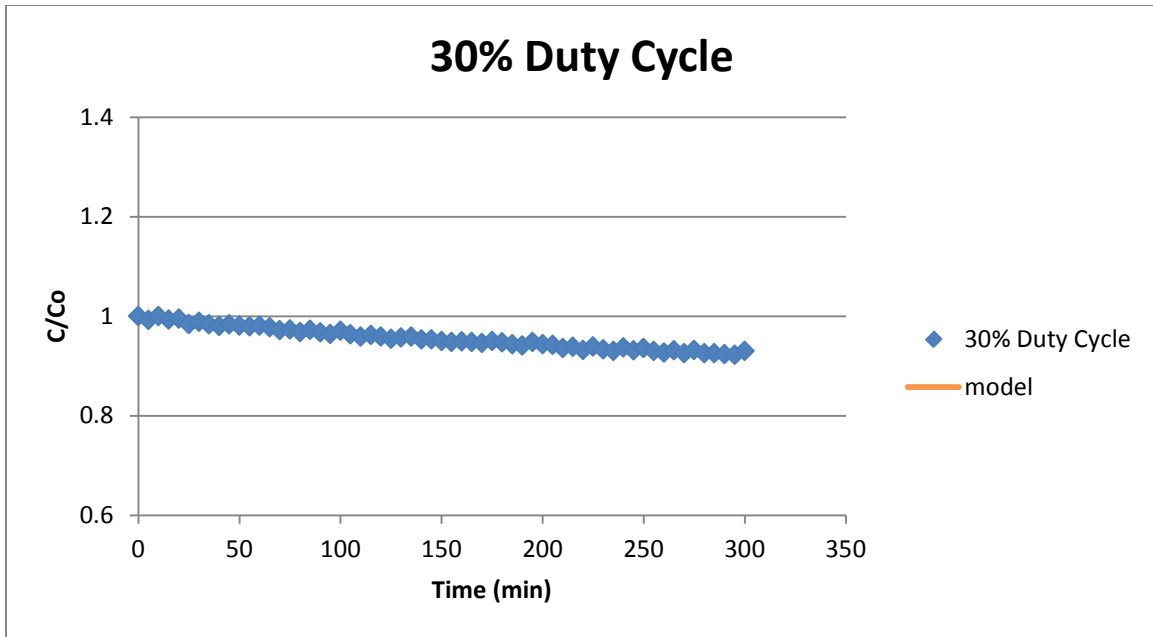
Appendix D. Raw Data for third experiment AOP for Tartrazine/H₂O₂ with UV LEDs

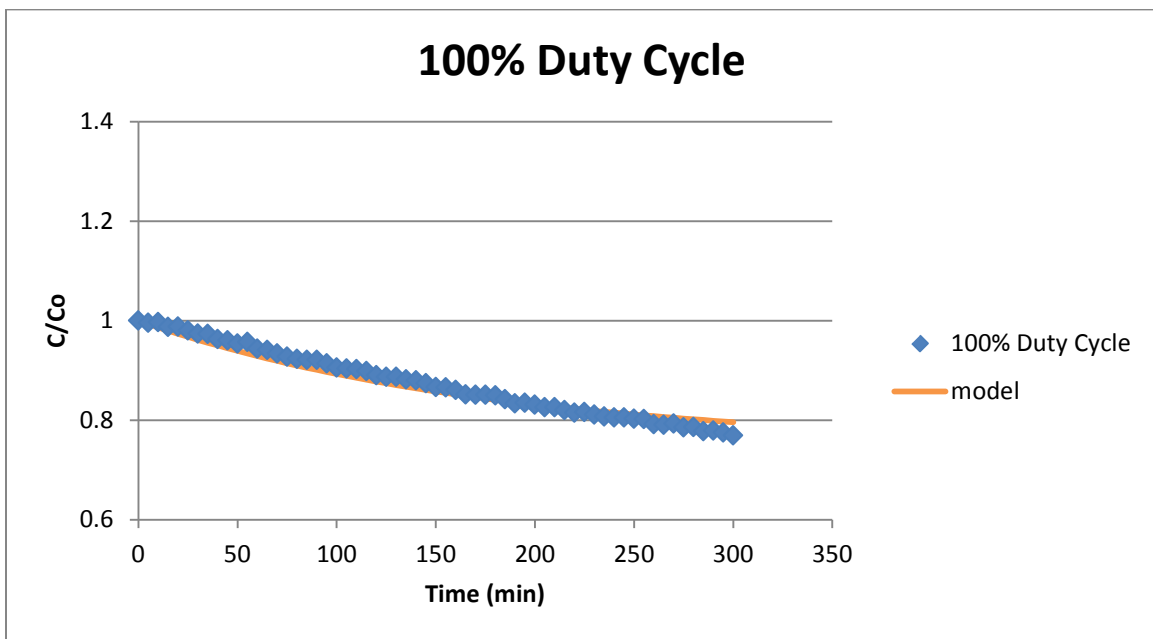
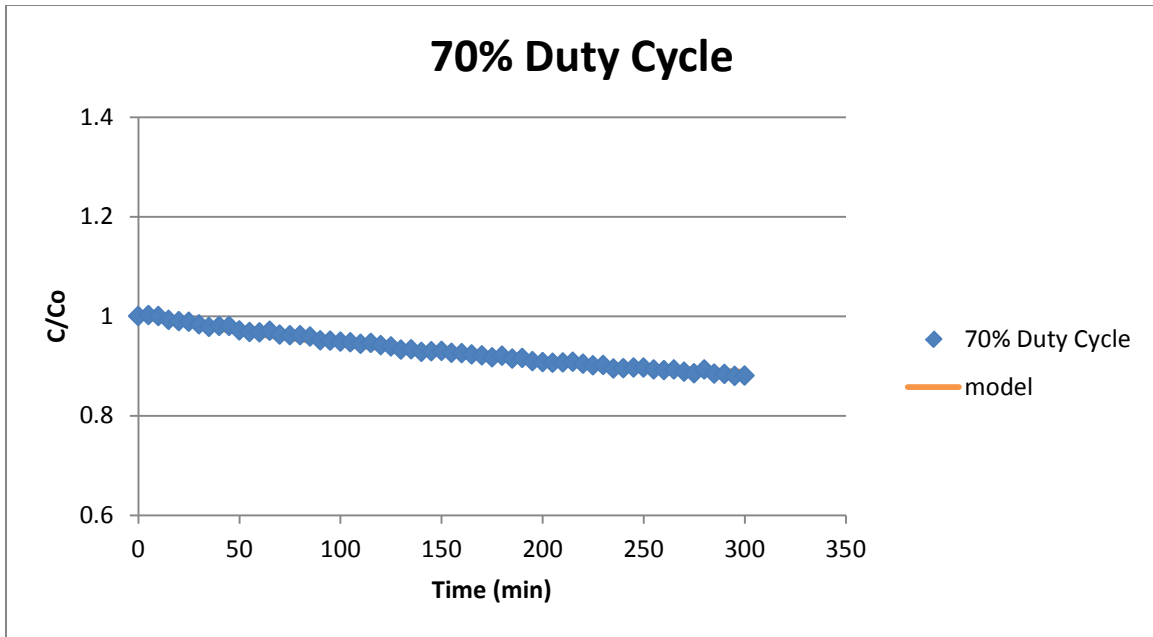




**Appendix E. Raw Data for fourth experiment AOP for Tartrazine/H₂O₂ with UV
LED**







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14. ABSTRACT A study was conducted to evaluate the advanced oxidation of organic contaminants using pulsed ultraviolet light emitted diode (UV LED). Tartrazine was used as a surrogate organic compound. Low pressure Mercury-based lamps currently used in the treatment of water pose potential health risks if broken and create final disposal issues at the end of their service life. UV LED offers an alternative solution due to its non-toxicity, flexible design, and longer operating life compared to the mercury-based lamps. The apparent first order reaction rate constant for tartrazine degradation increased linearly with increasing duty cycle. At a continuous 100% duty cycle, tartrazine degraded by 18% after 5 hours of operation. When normalized to power output, the lower duty cycles exhibited greater rate constants. The 5% duty cycle produced a normalized rate constant 100% greater than those observed at 20% and higher duty cycles. Reduced LED power output with time was not observed. As an anionic compound, it is believed tartrazine sorption to the LED surface was not occurring. Believed to be due to incomplete reactor mix, the experimental results show increased data noise at duty cycles 20% and greater. When the reactor was equipped with a mechanical mixing device, the data scatter was considerably reduced. Root square mean, R^2 , significantly improved from 0.57- 0.96 range for non-stirred reactor to 0.70 - 0.99 range for stirred reactor between 5% to 100% duty cycles.				
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